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(54) **TEXTILE PRINTING PASTE**

TEXTILDRUCKPASTE

PÂTE D'IMPRESSION POUR TEXTILE

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Description**Technical field**

5 **[0001]** The present invention deals with textile printing pastes comprising as thickener an enzymatically depolymerized polygalactomannan.

[0002] The fabrics printed with the textile printing pastes comprising an enzymatically depolymerized polygalactomannan show a higher colour strength and an excellent colour brightness, as demonstrated by an improved visual effect which is noticeable on the final article.

Background Art

[0003] Textile printing pastes serve to transfer dyes onto the fabric in a controlled way through a silk-screen, in order to have the correct formation of the desired pattern and decoration.

15 **[0004]** The textile printing paste composition is critical and largely determines the quality of the final article.

[0005] Printing pastes are prepared by solubilising a thickener in water and, successively, by adding the dye and other possible chemical auxiliaries useful to the process (such as pH regulators, antifoam agents, stabilisers and others) and have usually a solid content comprised between 4 and 20% by weight.

20 **[0006]** Commonly used thickeners are mainly composed by one or more water soluble natural or semisynthetic polymers of varying molecular weight, such as starch and its derivatives, alginates, polysaccharides from tamarind kernels, cellulose derivatives, polygalactomannans in general and polygalactomannans from guar seeds and their derivatives in particular.

[0007] The function of thickeners is to guarantee the viscosity to the paste in order to allow a better control in the pattern reproduction and sufficient fluidity for an easy passage through the silk-screen holes onto the fabric.

25 **[0008]** Depolymerized polygalactomannans are among the most used thickeners for printing with acid dyes on fabrics made of fibres like wool, silk and polyamide.

[0009] The expert in the field acknowledges that depolymerized polygalactomannans possess good characteristics in the typical printing process and can be promptly removed in the final washing phase.

30 **[0010]** Commercially available depolymerized polygalactomannans are obtained by reducing the molecular weight of natural polygalactomannans by chemical methods, such as using acids or alkalis, or, mainly, through the use of oxidative agents, i.e., hydrogen peroxide (as described for example in JP 03-290196).

[0011] Physical methods (using high speed agitation or various radiation sources), biochemical methods (wherein polysaccharide hydrolytic enzymes, bacteria, or fungi are used) and thermal methods are also known to reduce the molecular weight of polygalactomannans, but find limited applications on industrial scale.

35 **[0012]** For example, JP 1-020063 reports how to treat guar gum with hydrochloric acid at 40-70 °C in the presence of a cellulase or a pectinase to produce a hydrolyzed guar having Brookfield viscosity from 150 to 20,000 mPa.s at 5% by weight in water which can be used for food. It is doubtful whether the depolymerisation is driven by the acidic medium or by the presence of a non specific hydrolytic enzyme: indeed cellulase and pectinase are not able to break the 1-4 linkages between two mannose units.

40 **[0013]** JP 61-274695 describes how to detach the galactose branches from a guar with an alpha-galactosidase to make it suitable as dietary fiber or additive for dietary foods. The process taught by JP 61-274695 is not properly a depolymerisation, because the alpha-galactosidase acts on the lateral branches of the polygalactomannan and does not break its mannose backbone.

[0014] Purely enzymatic methods (i.e. no acids or alkalis or oxidizing agents used in conjunction with the enzyme) are described in the literature to furnish highly depolymerized polygalactomannan, which are not suitable as thickener.

45 **[0015]** JP 63-269993 describes that hardly digestible polysaccharides originated from vegetables such as guar gum are partially decomposed by a plant tissue hydrolytic enzyme having galactomannase activity to obtain a partially decomposed product having a viscosity of ≤ 10 mPa.s (measured by DVL-B type digital viscometer at 25 °C and 30 rpm and 1% aqueous solution) used as a dietary fiber or added to various dietary foods.

50 **[0016]** WO 99/04027 teaches how to obtain highly depolymerized polygalactomannans, particularly for food and pharmaceutical use (but also for oil field and personal care) by treating polygalactomannans splits with enzymes. Any suitable lytic enzyme is said to be utilizable: for example cellulase, hemicellulase, mannanase, galactomannanase, and even protease. Actually, the exemplified depolymerized polygalactomannans are obtained by treatment with a hemicellulase enzyme, have negligible viscosity in water and cannot be used as thickeners for textile printing pastes.

55 **[0017]** WO 2005/080668 deals with a thickener for printing pastes based on polygalactomannans derivatives and a protease, and with textile printing pastes containing said thickener. In this application it is said that the addition of said protease, permits to obtain printing pastes free from dotting caused by presence of proteins in the polygalactomannans. No mention is made about the possibility of depolymerizing the polygalactomannans.

[0018] It has now been found that polygalactomannans which have been properly depolymerized by enzymatic treatment may be used as thickeners in textile printing pastes and that, surprisingly, they provide improved properties to the printing pastes in which they are used.

[0019] In particular, it has been found that these printing pastes give improved colour brightness to a printed substrate and a higher yield of the dyes, when compared with those prepared using chemically depolymerized polygalactomannans.

[0020] The reason of this behaviour has not been deeply investigated, but possibly it may be due to the different molecular weight distribution deriving from the two different depolymerisation processes. Enzymatically depolymerized polygalactomannans show in gel permeation chromatography (GPC) a broad molecular weight distribution, almost bimodal, while chemically depolymerized polygalactomannans have a more narrow and regular distribution of the molecular weights.

[0021] With the expression "reducing end" we mean the end of a polysaccharide with a reducing anomeric carbon (C_1) that is not involved in a glycosidic bond. The content of reducing ends can be determined with different analytical techniques, such as spectrophotometry, gas-chromatography or 1H -NMR, and is expressed as μ moles of glucose per gram of polysaccharide.

Drawings

[0022] Figure 1 show a overlay chromatogram obtained by gel permeation chromatography of an enzymatically depolymerized guar polygalactomannan (dotted line) and of a same guar polygalactomannan depolymerized with a chemical agent (full line).

Summary of the invention

[0023] It is therefore an essential object of the present invention the use of enzymatically depolymerized polygalactomannans having a content of reducing ends comprised between 150 and 450 μ moles/g, preferably between 200 and 350 μ moles/g, and Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between 2 and 12% by weight, preferably between 4 and 12% by weight, in water as thickeners for textile printing pastes.

[0024] Another object of the invention is a textile printing paste comprising as thickener from 2.8 to 10%, preferably from 3.5 to 8%, by weight of an enzymatically depolymerized polygalactomannan having a content of reducing ends comprised between 150 and 450 μ moles/g, preferably between 200 and 350 μ moles/g, and Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between 2 and 12% by weight, preferably between 4 and 12% by weight, in water.

Detailed description of the invention

[0025] The enzymatically depolymerized polygalactomannans of the invention may be obtained by depolymerisation of polygalactomannans derived from various natural sources.

[0026] Preferably the polygalactomannan is guar, which is extracted from a leguminosae (*Cyamopsis tetragonoloba*) cultivated mainly in the arid and pre-desertic area between India and Pakistan.

[0027] In one preferred embodiment the polygalactomannan is guar in the form of flour.

[0028] In another embodiment the polygalactomannan is guar in the form of splits. Commercially available polygalactomannans different from guar may also be used to prepare the enzymatically depolymerized polygalactomannans. Examples of suitable polygalactomannans are those obtained from tara (tara gum), locust bean (locust bean gum), cassia (cassia gum), sesbania bispinosa (sesbania gum or daincha gum) and fenugreek (fenugreek gum).

[0029] In order to obtain the depolymerized polygalactomannans that can be used as thickeners for textile printing pastes, the polygalactomannan shall be treated with an endo- β -mannanase, such as Mannaway 4.0L from Novozymes and Rohalase GMP from AB enzymes. The depolymerisation reaction can be conducted, for example, by adding from 0.0001 to 20 part by weight each 100 part by weight of polygalactomannan of the mentioned commercial mannanase and stirring at a temperature comprised between 20 and 90 °C for from 1 to 24 hours.

[0030] Preferably, the polygalactomannan is treated with the enzyme in the presence of from 10 to 200 parts by weight of water each 100 parts by weight of polygalactomannan.

[0031] The enzymatic depolymerisation shall be carefully controlled to produce a depolymerized polygalactomannan having a content of reducing ends comprised between 150 and 450 μ moles/g, and Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between 2 and 12% by weight in water.

[0032] It is therefore necessary to inactivate the enzyme as soon as the depolymerized polygalactomannan has reached the desired viscosity, by way of example introducing a prolonged heating step, such as by heating for 1-5 hours at a temperature of 100 °C or higher, or by adding chemical inactivator such as N-bromosuccinimide or transition metal ions, for example Ag^+ ; Hg^{2+} , Zn^{2+} , Cu^{2+} .

[0033] The enzymatically depolymerized polygalactomannans of the invention are characterized by the content of reducing ends per gram of polygalactomannan, in fact the enzymatically depolymerized polygalactomannans show a higher number of reducing ends compared to a chemically depolymerized polygalactomannan with the same viscosity.

[0034] The textile printing pastes used in the present invention can include at least a dye. Dyes differ from pigment colorants in that they are used as liquid solutions, not as solid particle dispersions. In other words, dyes are typically completely soluble in water whereas pigment colorants are not. The enzymatically depolymerized polygalactomannan of the invention is particularly useful for the preparation of printing pastes containing acid dyes. According to a preferred embodiment, the textile printing pastes comprise acid dyes. More preferably, the textile printing pastes contain from 0.1 to 10% by weight of one or more acid dyes.

[0035] Examples of suitable acid dyes can be chosen among the group of anthraquinone type dyes, such as Colour Index (CI) Acid Blue 43 or CI Acid Blue 129, the azo-dyes, such as CI Acid Red 88 or CI Acid Red 114, and triphenylmethane dyes, such as CI Acid Violet 17, CI Acid Blue 15, CI Acid Blue 7 and CI Acid Green 3. Particularly preferred are premetallized acid dyes, for example CI Acid Blue 193 or CI Acid black 194.

[0036] The textile printing paste according to the invention can further contain one or more other polymer having thickening function, chosen among alginates, starch and its derivatives, tamarind derivatives, synthetic polymers, cellulose derivatives, polygalactomannan derivatives, such as hydroxypropyl polygalactomannan and carboxymethyl polygalactomannan, preferably in a quantity not higher than 4% by weight.

[0037] The textile printing paste according to the invention can further comprise textile printing additives familiar to the expert, such as wetting agents, emulsifiers, dispersing agents; solubilizing agents; defoamers; reducing agents, oxidizing agents, resist agents, pH regulators, complexing agents, preservatives; and mixture thereof.

[0038] Wetting agents, emulsifiers, dispersing agents can be anionic, cationic or nonionic in a known manner. Examples of these are: reaction products of aliphatic, araliphatic or aromatic hydroxy compounds, carboxylic acids, carboxylic acid amides or amines with ethylene oxide; sulfuric acid half esters or phosphoric acid partial esters thereof; fatty acid esters of mono- or polysaccharides or fatty acid sorbitan esters and ethoxylation products thereof; C₁₀-C₂₀ -alkanesulfonates, C₈-C₁₂ alkylbenzenesulfonates; C₈-C₁₈ alkyl sulfates or phosphates; or condensed aromatic sulfonic acids, such as naphthalene-formaldehyde-sulfonates. Substances of the type mentioned can also serve as leveling agents.

[0039] Solubilizing agents as further additives are, for example, glycols, mono- to tetraalkyleneglycols and ethers or esters thereof with C₁-C₄ alcohols or C₁-C₄ carboxylic acids.

[0040] Defoamers are, for example, compositions comprising vegetable oils or mineral oils or, in particular, propylene oxide/ethylene oxide block polymers. The textile printing additives mentioned in the preceding paragraphs can be present in an amount of 0 to 10% by weight, based on the total weight of the pastes according to the invention.

[0041] The textile printing pastes of the invention can be prepared according to the usual procedures, by slowly adding the thickener(s) to water, under mechanical stirring, until complete dissolution is achieved, and by adding to the thickener solution the additives (pH regulators, antifoam, and so on) and the dye, and finally by adding water up to the desired concentration of active substances.

[0042] In the printing process of the invention, the textile materials are subjected to printing using essentially any textile screening techniques known in the art. One common technique is silk screen printing where the paste is applied to the surface of the fabric by pressing the paste through screens. The screens are conventionally made of silk, but any screen suitable for silk screen printing can be utilized, for example in nylon or polyester. Rotary screen printing and flat (bed) screen printing are examples of industrially applicable printing techniques. Inkjet printing for textile material is also suitable for the realization of the invention.

[0043] Textile materials which can be printed using the pastes according to the invention are fiber materials of loose fibers, woven or knitted goods or those in the form of nonwovens, based on natural or synthetic fibers or mixtures thereof. Examples of natural fibers are wool, silk, linen, as well as jute. Examples of synthetic fibers are polyamides, polyacrylonitriles or polypropylenes.

Examples

Test methods

[0044] The viscosity of the solutions was measured 2 hours after the dissolution of the depolymerized polygalactomannans with a DV-E Brookfield® viscometer at 20°C and at 20 rpm.

[0045] Gel permeation chromatography (GPC) was performed by dissolving the depolymerized guar samples at a concentration of 0.3 g of sample in 100 ml of 0.10 M ammonium acetate ("mobile phase solution"). Two hundred microliters of each solution, filtered on a 0.45 micron membrane filter were injected into a HPLC equipped with a evaporative light scattering detector. The following columns were used at a temperature of 60 °C: Supelco Progel -TSK G3000 PWXL, Progel-TSK G6000 PWXL, and Progel-TSK PWXL guard column. The HPLC was set at a flow rate of 0.8 ml/min for 50 minutes.

[0046] The content of reducing ends of the polygalactomannans was determined according to Zhang, P. Y. and Lynd, L. R., *Biomacromolecules* 6, 1510-1515 (2005).

[0047] The strength of the colours of the printed fabrics was evaluated instrumentally using a DataColor Int. reflectance spectrophotometer (Spectral Test SE600 PLUS-CT) under a DL65/10° illuminant. The (K/S) values were calculated according to AATCC Evaluation Procedure 6.

Examples 1-5

[0048] Enzymatically depolymerized polygalactomannan (Examples 1-3) were prepared by mixing 100 g of different guar flours with 0.5 g of Mannaway 4.0L (Novozymes) and 150 g of water and heating at 60 °C. After 60 minutes the temperature was increased to 100 °C for other 60 min for the denaturation of the enzyme. The obtained product was dried in a fluidized bed at 80 °C for 60 minutes and then milled into powder form. The final moisture content of the powders was about 10-12% by weight.

[0049] For comparison a guar flour depolymerized with NaOH and hydrogen peroxide was used (Example 4).

[0050] Table 1 reports the concentration (% by weight) in water at which the Brookfield® viscosity is 20,000 mPa·s and the amount of reducing ends of the depolymerized polygalactomannans utilized in the printing test and of an unmodified guar flour (Example 5).

Table 1

Sample	Concentration (% wt)	Reducing ends (μmoles/g)
Example 1	7.0	210
Example 2	9.5	289
Example 3	9.9	323
Example 4*	11.0	70.4
Example 5*	1.6	89.0
* Comparative		

PRINTING TEST

Visual evaluation

[0051] The amount of thickeners of Examples 1-4 required to reach a viscosity of 20,000 mPa·s were added, under mechanical stirring, to 91 g of water and mixed until complete dissolution (about 40 min). The solutions were allowed to rest for about half an hour.

[0052] 50 g of thiodiglycol and 50 g of urea were weighed in a 1000 ml beaker and carefully mixed. The mixture was dissolved by pouring under stirring boiling water to obtain 1000 g of solution. The solution was then filtered on a polyester canvas of 54 micron.

[0053] 60 g of thickener solution were carefully homogenized with 40 g of the solution containing thiodiglycol and urea under mechanical stirring. Subsequently 2.0 g of (NH₄)₂SO₄ were added, under stirring, in order to control the pH during the colour fixing phase.

[0054] A white silk fabric was printed with the printing pastes prepared with the depolymerized polygalactomannans of Examples 1-4 by using an appropriate 77 threads/cm silk screen (5 stripes 5x40 cm design) and a Zimmer laboratory printing machine set at speed 4 and pressure 2. A 4 mm steel rod was used.

[0055] The fabric so obtained was then dried at a temperature of 90°C for 1 minute in oven and treated for 40 minutes, for fixing, in an Arioli vaporising machine set at 102 °C. The printed fabric was washed at 30 °C in the presence of soap, dried and finally ironed.

[0056] The appearance of the printed fabrics were visually evaluated. The area printed with the pastes according to the invention were whiter than the area printed with the comparative paste.

[0057] The printing tests were repeated, using the same ingredients and following the same printing procedure, but adding 30 g of Red Tiacidol GRE or Dark Blue Tiasolan LB (acid dyes commercialized by Lamberti SpA) in the thiodiglycol and urea solution.

[0058] The appearance of the dyed printed fabrics were visually evaluated. The area printed with the pastes according to the invention showed colour with a superior brightness compared with the area printed with the comparative paste.

Instrumental evaluation

[0059] The printing tests were repeated following the same printing procedure reported above, using the thickeners of Example 2 and comparative Example 4, the same other ingredients, but adding 30 g of Yellow Tiacidol K- 5GN (acid dye commercialized by Lamberti SpA) in the thiodiglycol and urea solution.

[0060] Table 2 shows the colour strenght (K/S) of the silk fabrics printed using the paste of Example 2 (front area and back area) and of the fabric printed using the paste of comparative Example 4 (front area and back area). The percent increase of K/S is also reported.

Table 2

	K/S front	% Increase K/S	K/S back	% Increase K/S
	(wavelength 420 nm)			
Example 4*	7.80	-	4.57	-
Example 1	9.38	20,27	5.75	25.83
* Comparative				

Claims

1. Use as thickeners for textile printing pastes of enzymatically depolymerized polygalactomannans having a content of reducing ends comprised between 150 and 450 μ moles/g and Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between 2% and 12% by weight in water.
2. The use according to Claim 1) wherein said enzymatically depolymerized polygalactomannans have a content of reducing ends comprised between 200 and 350 μ moles/g.
3. The use according to Claim 1) wherein said enzymatically depolymerized polygalactomannans have Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between between 4% and 12% by weight in water.
4. Textile printing paste comprising as thickener from 2.8% to 10% by weight of an enzymatically depolymerized polygalactomannan having a content of reducing ends comprised between 150 and 450 μ moles/g and Brookfield® viscosity at 20°C and 20 rpm of about 20,000 mPa.s at a concentration comprised between 2% and 12% by weight in water.
5. The textile printing paste according to Claim 4) comprising from 3.5% to 8% of said enzymatically depolymerized polygalactomannan.
6. The textile printing paste according to Claim 4) comprising from 0.1 % to 10% by weight of one or more acid dyes.
7. The textile printing paste according to Claim 4), further comprising up to 4% by weight of one or more polymers having thickening function chosen among alginates, starch and its derivatives, tamarind derivatives, synthetic polymers, cellulose derivatives and polygalactomannan derivatives.
8. The textile printing paste according to Claim 4), further comprising up to 10% by weight of one or more additives chosen among wetting agents, emulsifiers, dispersing agents; solubilizing agents; defoamers; reducing agents, oxidizing agents, resist agents, pH regulators, complexing agents, preservatives and mixture thereof.

Patentansprüche

1. Verwendung enzymatisch depolymerisierter Polygalactomannane, die einen Gehalt an reduzierenden Enden zwischen 150 und 450 μ mol/g und eine Brookfield-Viskosität bei 20 °C und 20 UpM von etwa 20 000 mPa.s bei einer Konzentration zwischen 2 und 12 Gew.-% in Wasser haben, als Verdickungsmittel in Textildruckpasten.

2. Verwendung nach Anspruch 1, wobei die enzymatisch depolymerisierten Polygalactomannane einen Gehalt an reduzierenden Enden zwischen 200 und 350 $\mu\text{mol/g}$ haben.
3. Verwendung nach Anspruch 1, wobei die enzymatisch depolymerisierten Polygalactomannane eine Brookfield-Viskosität bei 20 °C und 20 UpM von etwa 20 000 mPa.s bei einer Konzentration zwischen 4 und 12 Gew.-% in Wasser haben.
4. Textildruckpaste, umfassend 2,8 bis 10 Gew.-% enzymatisch depolymerisiertes Polygalactomannan, das einen Gehalt an reduzierenden Enden zwischen 150 und 450 $\mu\text{mol/g}$ und eine Brookfield-Viskosität bei 20 °C und 20 UpM von etwa 20 000 mPa.s bei einer Konzentration zwischen 2 und 12 Gew.-% in Wasser hat, als Verdickungsmittel.
5. Textildruckpaste nach Anspruch 4, die 3,5 bis 8 % enzymatisch depolymerisiertes Polygalactomannan aufweist.
6. Textildruckpaste nach Anspruch 4, die 0,1 bis 10 Gew.-% eines oder mehrerer Säurefarbstoffe aufweist.
7. Textildruckpaste nach Anspruch 4, die ferner bis zu 4 Gew.-% eines oder mehrerer Polymere mit Verdickungsfunktion aufweist, ausgewählt aus Alginaten, Stärke und ihren Derivaten, Tamarinde-Derivaten, synthetischen Polymeren, Cellulose-Derivaten und Polygalactomannan-Derivaten.
8. Textildruckpaste nach Anspruch 4, die ferner bis zu 10 Gew.-% eines oder mehrerer Additive aufweist, ausgewählt aus Netzmitteln, Emulgakoren, Dispergiermitteln; Lösungsvermittlern; Entschäumern; Reduktionsmitteln, Oxidationsmitteln. Reservierungsmitteln, pH-Regulatoren, Komplexierungsmitteln, Konservierungsmitteln und Mischungen davon.

Revendications

1. Utilisation à titre d'agents épaississants de pâtes d'impression pour textiles de polygalactomannanes dépolymérisés par voie enzymatique ayant une teneur en extrémités réductrices comprise entre 150 et 450 $\mu\text{moles/g}$ et une viscosité Brookfield® à 20 °C et 20 tours/min d'environ 20 000 mPa.s à une concentration comprise entre 2 et 12 % en poids dans l'eau.
2. Utilisation selon la revendication 1) dans laquelle lesdits polygalactomannanes dépolymérisés par voie enzymatique ont une teneur en extrémités réductrices comprise entre 200 et 350 $\mu\text{moles/g}$.
3. Utilisation selon la revendication 1) dans laquelle lesdits polygalactomannanes dépolymérisés par voie enzymatique ont une viscosité Brookfield® à 20 °C et 20 tours/min d'environ 20 000 mPa.s à une concentration comprise entre 4 et 12 % en poids dans l'eau.
4. Pâte d'impression pour textiles comprenant à titre d'agent épaississant de 2,8 à 10 % en poids d'un polygalactomannane dépolymérisé par voie enzymatique ayant une teneur en extrémités réductrices comprise entre 150 et 450 $\mu\text{moles/g}$ et une viscosité Brookfield® à 20 °C et 20 tours/min d'environ 20 000 mPa.s à une concentration comprise entre 2 et 12 % en poids dans l'eau.
5. Pâte d'impression pour textiles selon la revendication 4 comprenant de 3,5 à 8 % en poids dudit polygalactomannane dépolymérisé par voie enzymatique.
6. Pâte d'impression pour textiles selon la revendication 4 comprenant de 0,1 à 10 % en poids d'un ou de plusieurs colorants acides.
7. Pâte d'impression pour textiles selon la revendication 4, comprenant en outre jusqu'à 4 % en poids d'un ou de plusieurs polymères ayant une fonction épaississante choisis parmi les alginates, l'amidon et ses dérivés, les dérivés de tamarin, les polymères synthétiques, les dérivés cellulosiques et les dérivés de polygalactomannane.
8. Pâte d'impression pour textiles selon la revendication 4, comprenant en outre jusqu'à 10 % en poids d'un ou de plusieurs additifs choisis parmi les agents de mouillage, les émulsifiants, les agents de dispersion ; les agents solubilisants ; les anti-mousse ; les agents réducteurs, les agents oxydants, les agents de réserve, les régulateurs de pH, les agents complexants, les conservateurs et leur mélange.

REFERENCES CITED IN THE DESCRIPTION

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