

Description

Different gum blends are widely known and used. Generally celluloseics were found to be incompatible with xanthan gum, owing to the presence in the latter of various cellulase enzymes. Moreover, although celluloseics are widely used, they suffer to varying degrees in different applications from salt incompatibility, instability to heat, limited shelf life, instability to pH changes, and unpleasant or undesirable mouth-feel in certain compositions such as toothpaste. However, if celluloseics were mixed with many other gums in order to improve these characteristics, the final viscosity was usually detrimentally affected.

The present invention results from the unexpected discovery that celluloseics, including carboxymethylcellulose, hydroxyethylcellulose and hydroxypropylmethylcellulose, can be mixed with cellulase-free xanthan gum to give blends that show unusual synergism. Such blends are provided by this invention. The quantities of gum and celluloseic preferably range from a 1:3 to 3:1 weight basis, i.e. from 9 to 1 parts of gum to 3 parts by weight of the celluloseic.

In blends in accordance with the present invention, not only are the desirable properties of the celluloseics retained and the undesirable properties of celluloseics minimized, but the resulting viscosities of the solutions prepared from these blends are surprisingly and unexpectedly higher than that predictable from measurements of either component alone.

The synergistic effect can be demonstrated in synthetic tap water (STW) on 1:1 (weight basis) blends, thereby keeping the good qualities of celluloseics with a 50% dilution, and the good qualities of xanthan gum at 50% dilution, while maintaining and even increasing viscosity of solutions of these 1:1 blends. The synergistic effect in viscosity can be demonstrated at 1%, 0.5%, 0.25% and 0.1% concentration levels in Synthetic Tap Water (STW); the synergism is not as pronounced in deionized water.

The celluloseics useful in this invention are all the commercially available forms of celluloseics, including carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose.

The cellulase-free xanthan gum can be any of a number of grades available. One form is produced by treating xanthan gum beer with an alkali metal hypochlorite of pH 6 to 7 at concentration levels of 0.08—0.1% by weight and about 30°C for 6—8 hours, followed by heating to 85—95°C for several minutes, then recovering, by precipitating the cellulase-free beer, and by drying and milling the presscake. Other methods include treatment of xanthan gum beer with mercury compounds, treatment of xanthan gum beer presscakes with propylene oxide, and heating xanthan gum beer that has been adjusted to high pH to about 90°C followed by cooling and neutralization.

The two gums are dry blended, at about a 1:1 weight ratio, by rolling or any other such technique. Another method involves adding the desired celluloseic to cellulase-free xanthan gum beer, and then recovering the blend using the normal recovery steps for xanthan gum alone.

These blends can be used in any formulation where celluloseics are used, such as toothpastes or drink mixes. A formulation for toothpaste using this blend follows:

Toothpaste		
	%	gm
Sorbitol	12.5	500
Glycerol	12.5	500
DCPD (dicalcium phosphate dihydrate)	45.0	1800
Sodium lauryl sulphate	1.5	60
Methylparaben	0.15	6
Titanium dioxide	0.75	30
Saccharin	0.15	6
Flavour	1.0	40
Colour	0.02	0.8
Water	25.43	1017.2
Carboxymethylcellulose	0.5	20
Xanthan gum, cellulase-free	0.5	20
	100.0%	4000 g

The final toothpaste was completely suitable.

Determination of synergism

Data were determined for 1%, 0.5%, 0.25%, and 0.1% concentration of a 1:1 blend of the indicated gums. Two methods were used to calculate theoretical expected values, one the log-plot (see U.S. Patent No. 4,169,818 for reference to this method) the other, the sum of 1/2 viscosities. Values were also calculated by mathematical average, but these were not considered as reliable and are not included. The data are summarized in Tables I, II, III and IV. Viscosities are given in mPa . s, which are equivalent to centipoises.

TABLE I:
% Synergism of cellulase-free XG with cellulose in
STW¹: 1.0% total solids
Blend viscosity (1:1)

Sample	Gum viscosity		Blend viscosity (1:1)		% Synergism ³
	0.5% Viscosity/STW	1.0% Viscosity/STW	Viscosity A Experimental	Viscosity B Theoretical value ²	
Carboxymethyl-cellulose, 7HOF	92.5	626	1150	a) 995 b) 622.5	+16 +85
Hydroxyethyl-cellulose, QP4400	57.5	550	1220	a) 935 b) 587.5	+30 +108
Hydroxypropyl-methyl cellulose, Methocel, 90HG	20.5	115	1000	a) 500 b) 550.5	+100 +82
Cellulase-free xanthan gum (produced by hypochlorite treatment)	530	1586	—	—	—

¹ synthetic tap water—1000 ppm NaCl & 143 ppm CaCl₂ · 2H₂O in D.I. water.

² a) calculated from log-plot of 1.0% viscosities.

b) calculated from sum of 0.5% viscosities.

³ % synergism = $\frac{\text{Viscosity A} - \text{Viscosity B}}{\text{Viscosity B}} \times 100$

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TABLE II:
% Synergism of cellulase-free XG with cellulose in
STW¹: 0.5% total solids
Blend viscosity (1:1)

Sample	Gum viscosity		Blend viscosity (1:1)		% Synergism ³
	0.25%	0.5%	Viscosity A	Viscosity B	
	Viscosity/STW	Viscosity/STW	Experimental	Theoretical value ²	
10 Carboxymethyl-cellulose, 7HOF	19.5	84.5	247.5	a) 198 b) 154.5	+25 +60
Hydroxyethyl-cellulose, QP4400	10	40	230	a) 136 b) 142	+69 +59
15 Hydroxypropyl-methyl cellulose Methocel, 90HG	7	20.5	200	a) 98 b) 142	+104 +41
20 Cellulase-free xanthan gum (produced by hypochlorite treatment)	135	466.3	—	—	—

¹ Synthetic tap water—1000 ppm NaCl and 143 ppm CaCl₂ · 2H₂O in D.I. water.

² a) calculated from log-plot of 0.5% viscosities

b) calculated from sum of 0.25% viscosities.

$$30 \quad ^3 \% \text{ synergism} = \frac{\text{Viscosity A} - \text{Viscosity B}}{\text{Viscosity B}} \times 100$$

TABLE III:
% Synergism of cellulase-free XG with cellulose in
STW¹: 0.25% total solids
Blend viscosity (1:1)

Sample	Gum viscosity		Blend viscosity (1:1)		% Synergism ³
	0.125%	0.25%	Viscosity A	Viscosity B	
	Viscosity/STW	Viscosity/STW	Experimental	Theoretical value ²	
40 Carboxymethyl-cellulose, 7HOF	7.8	19.5	56.5	a) 52 b) 48.4	+9 +17
45 Hydroxyethyl-cellulose, QP4400	3.25	10	50	a) 37 b) 43.85	+35 +14
50 Hydroxypropyl-methyl cellulose, Methocel 90HG	3.8	7	44.5	a) 31 b) 44.4	+44 +0.2
55 Cellulase-free xanthan gum (produced by hypochlorite treatment)	40.6	135	—	—	—

¹ Synthetic tap water—1000 ppm NaCl and 143 ppm CaCl₂ · 2H₂O in D.I. water.

² a) calculated from log-plot of 0.25% viscosities.

b) calculated from sum of 0.125% viscosities.

$$60 \quad ^3 \% \text{ synergism} = \frac{\text{Viscosity A} - \text{Viscosity B}}{\text{Viscosity B}} \times 100$$

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TABLE IV:
% Synergism of cellulase-free XG with cellulose in
STW¹: 0.1% total solids
Blend viscosity (1:1)

Sample	Gum viscosity		Blend viscosity (1:1)		% Synergism ³
	0.05%	0.1%	Viscosity A	Viscosity B	
	Viscosity/STW	Viscosity/STW	Experimental	Theoretical value ²	
10 Carboxymethyl-cellulose, 7HOF	3.5	6.5	15.0	a) 14.3 b) 12.5	+5 +20
Hydroxyethyl-cellulose, QP4400	2.5	3.9	12.5	a) 11.0 b) 11.5	+14 +9
15 Hydroxypropyl-methyl cellulose, Methocel, 90HG	4.0	6.0	16.0	a) 13.6 b) 13.0	+18 +23
20 Cellulase-free xanthan gum (produced by hypochlorite treatment)	9.0	31.5	—	—	—

¹ Synthetic tap water—1000 ppm NaCl and 143 ppm CaCl₂ · 2H₂O in D.I. water.

² a) calculated from log-plot of 0.1% viscosities.

b) calculated from sum of 0.05% viscosities.

30 ³ % synergism = $\frac{\text{Viscosity A} - \text{Viscosity B}}{\text{Viscosity B}} \times 100$

35 Other data were obtained by dissolving the dry gum powder blends (1:1) in 1% KCl and viscosities (1% total solids) measured using a Brookfield LVF viscometer, spindle No. 3 at 60 rpm, and are shown in Table V.

TABLE V:
% Synergism of cellulase-free XG with cellulose in
1% KCl: 1% total solids
Blend viscosity (1:1)

Sample	Gum viscosity	Blend viscosity (1:1)		% Synergism ²
	1% Viscosity/KCl	Viscosity A	Viscosity B	
45 Carboxymethyl-cellulose, 7HOF	860	1180	1150	3
50 Hydroxyethyl-cellulose	310	820	680	21
55 Hydroxypropyl-methylcellulose Methocel 90HG	180	780	520	50
60 Cellulase-free xanthan gum	1500	—	—	—

¹ calculated from log plots of 1.0% viscosities.

65 ² % synergism = $\frac{\text{Viscosity A} - \text{Viscosity B}}{\text{Viscosity B}} \times 100$

Claims

1. A blend of cellulase-free xanthan gum and either carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylmethylcellulose.
2. A blend as claimed in Claim 1 containing from 9 to 1 parts by weight of the gum to 3 parts by weight of the cellulose derivative.
3. A blend as claimed in Claim 2 in which equal weights of carboxymethylcellulose and xanthan gum are used.
4. A blend as claimed in Claim 2 in which equal weights of hydroxyethylcellulose and xanthan gum are used.
5. A blend as claimed in Claim 2 in which equal weights of hydroxypropylmethylcellulose and xanthan gum are used.
6. A 1:3 (weight basis) blend of cellulase-free xanthan gum and either carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylmethyl cellulose.
7. A 3:1 (weight basis) blend of cellulase-free xanthan gum and either carboxymethyl cellulose, hydroxyethyl cellulose, or hydroxypropylmethyl cellulose.

Patentansprüche

1. Mischung aus cellulasefreiem Xanthangummi und entweder Carboxymethylcellulose, Hydroxyethylcellulose oder Hydroxypropylmethylcellulose.
2. Mischung nach Anspruch 1, enthaltend 9 bis 1 Gewichtsteile des Gummis pro 3 Gewichtsteile des Cellulosederivats.
3. Mischung nach Anspruch 2, in der gleiche Gewichte an Carboxymethylcellulose und Xanthangummi verwendet werden.
4. Mischung nach Anspruch 2, in der gleiche Gewichte an Hydroxyethylcellulose und Xanthangummi verwendet werden.
5. Mischung nach Anspruch 2, in der gleiche Gewichte an Hydroxypropylmethylcellulose und Xanthangummi verwendet werden.
6. Eine 1:3 (Gewichtsbasis) Mischung aus cellulasefreiem Xanthangummi und entweder Carboxymethylcellulose, Hydroxyethylcellulose oder Hydroxypropylmethylcellulose.
7. Eine 3:1 (Gewichtsbasis) Mischung aus cellulasefreiem Xanthangummi und entweder Carboxymethylcellulose, Hydroxyethylcellulose oder Hydroxypropylmethylcellulose.

Revendications

1. Mélange de gomme xanthanique exempte de cellulase, et de carboxyméthylcellulose, hydroxyéthylcellulose ou hydroxypropylméthylcellulose.
2. Mélange selon la revendication 1, contenant de 9 à 1 parties en poids de la gomme pour 3 parties en poids du dérivé cellulosique.
3. Mélange selon la revendication 2, dans lequel on utilise des poids égaux de carboxyméthylcellulose et de gomme xanthanique.
4. Mélange selon la revendication 2, dans lequel on utilise des poids égaux d'hydroxyéthylcellulose et de gomme xanthanique.
5. Mélange selon la revendication 2, dans lequel on utilise des poids égaux d'hydroxypropylméthylcellulose et de gomme xanthanique.
6. Mélange (1:3 en poids) de gomme xanthanique exempte de cellulase et de carboxyméthylcellulose, hydroxyéthylcellulose ou hydroxypropylméthylcellulose.
7. Mélange (3:1 en poids) de gomme xanthanique exempte de cellulase et de carboxyméthylcellulose, hydroxyéthylcellulose ou hydroxypropylméthylcellulose.

