

The Effect of Thermal Aging on Xanthan Solutions

M. MILAS, *Centre de Recherches sur les Macromolécules Végétales CNRS, Laboratoire Propre du CNRS, Associé à l'Université Scientifique, Technologique et Médicale de Grenoble, B.P. 68-38402 Saint-Martin d'Hères Cedex, France*, and J. L. LIHOSSIER and F. CONTAT, *Rhône-Poulenc Recherches, Centre d'Industrialisation de Décines, 24 Avenue Jean Jaurès 69151, Décines, France*

Synopsis

The viscosity stability of xanthan solutions is crucial to petroleum recovery processes. The effects of oxygen concentration, pH, and temperature on viscosity during aging up to 6 months were studied. The structure modifications of the xanthan (substituent contents, weight-average molecular weights) with aging times were followed and related to viscosity loss. In all cases, the acetyl groups were hydrolyzed. The best stability to thermal aging corresponds to neutral or basic conditions with very low oxygen concentrations. At these conditions the viscosity was stabilized to about 50% of its initial value after 6 months at 80°C. In these cases the pyruvate groups were not hydrolyzed. The stabilization of main chain breaks in the ordered xanthan conformation improves the stability results.

INTRODUCTION

Many authors have shown that xanthan can be used in tertiary oil recovery because of its viscous and viscoelastic properties.^{1,2} However, many problems exist because of plugging behavior and poor viscosity stability at high temperature. Chemical treatment,³ enzymatic treatment,⁴⁻⁶ or the preferential use of fermentation broth⁷ have been proposed to prevent plugging. Concerning viscosity stability, it is well known that it is improved if xanthan contains an ordered conformation.⁸⁻¹⁰ However, at elevated temperatures, chemical depolymerization can occur^{11,12} as well as biodegradation.¹³ Only a few studies have been carried out to improve the viscosity stability in tertiary oil recovery conditions.^{14,15} The aim of this work is to follow viscosity, the weight-average molecular weight (\bar{M}_w), and the substituent contents in xanthan after treatment with different additives as a function of time and temperature.

EXPERIMENTAL

We have used a xanthan broth from Rhône-Poulenc with a xanthan concentration, given by the manufacturer, equal to about 68.5 g/kg. The xanthan broth was diluted by a factor of 68.5; thus the xanthan concentration was approximately 1 g/L for these experiments. Because oxygen can be a source of polymer degradation, it is removed by sparging the solution with oxygen-free

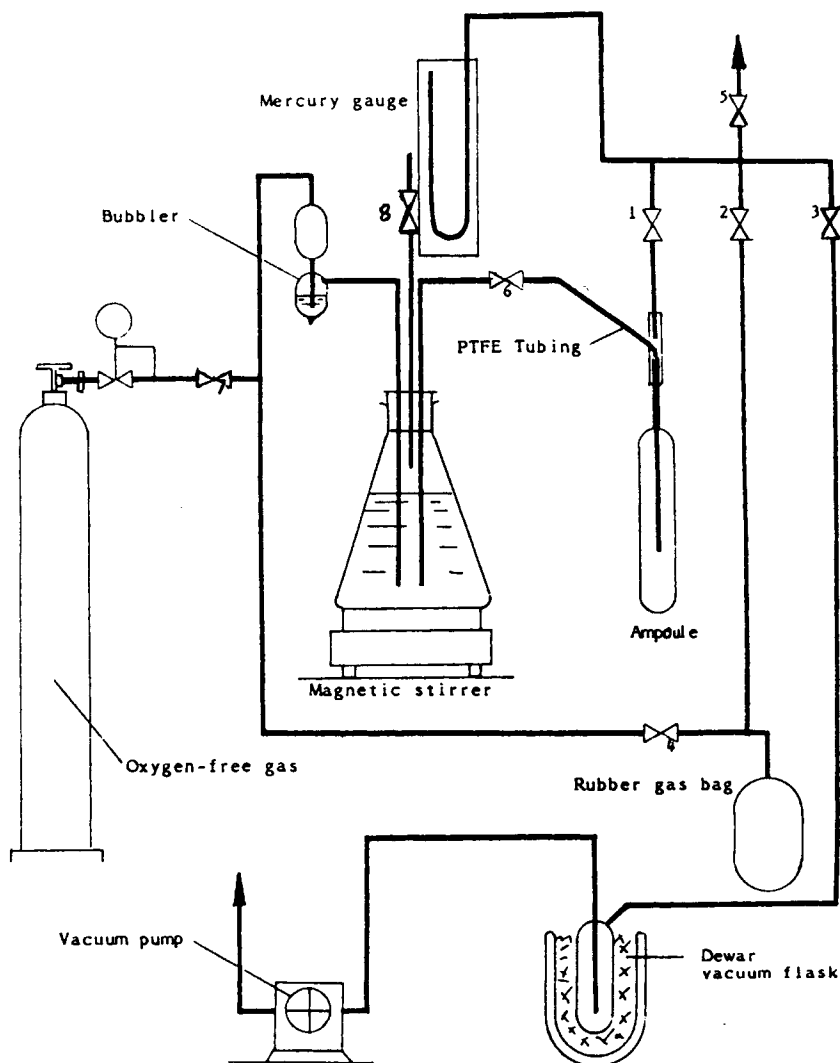


Fig. 1. Drawing of the apparatus used for sparging the xanthan solution and filling the test ampoules:

| Valve number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-------------------------------|---|---|---|---|---|---|---|---|
| Sparging | C | C | C | C | C | C | O | O |
| Filling of the rubber gas bag | C | C | C | O | C | C | O | C |
| Vacuum in the ampoule | O | C | O | C | C | C | C | C |
| Filling the ampoule | C | C | C | C | C | O | C | C |
| Decreasing vacuum | O | O | C | C | C | C | C | C |

5 = general purge valve; C = valve closed, O = valve open.

gas (He, CO₂, or N₂) or/and oxygen scavengers (hydrazin or sodium sulfite). Formaldehyde, 2,4,6-sodium trichlorophenate (2,4,6,T) or 2-butanol were used as bactericides. For industrial applications like tertiary oil recovery, external salts are often present. Thus NaCl, MgCl₂, and CaCl₂ were added to the xanthan solution to take into account their contributions. Other additives with the exception of oxygen scavengers, were then added. The 100-mL glass ampoules were filled by using the apparatus described in the Figure 1. Oxygen is removed by sparging the solution with an oxygen-free gas, for about 12 h. Just before sealing the ampoules, oxygen scavengers were added to the solution. The ampoules were filled by vacuum. Atmospheric pressure inside the ampoules was restored with the oxygen-free gas and the ampoule was sealed by melting the neck with a blowtorch. The ampoules were stored in ovens at the selected temperatures (40, 60, and 80°C) for 2 and 6 months.

Oxygen levels were measured using auto-filling CHEMest ampoules (Chemetrics, Inc.). The top of the ampoules, containing the polysaccharide solution, was broken. Immediately after this operation, the tip of the CHEMest ampoule was broken in the polysaccharide solution, and the vacuum inside the CHEMest ampoule sucked the polysaccharide solution into it. Then the contents of the CHEMest ampoule were mixed by tilting and allowing the small bubbles to travel from end to end several times. After allowing time for full-color development, a comparator was used to determine the test result. For low O₂ content (< 50 ppb), the precision can be estimated to about ±10 ppb. Next the pH and the viscosity were measured, and the results are given in Table I. Since the difference by sparging the solution with He, N₂, or CO₂ was hardly noticeable, Table I contains only the results obtained with CO₂. After filtration through 3-μm Millipore filter (type SS), the xanthan was recovered by precipitation by ethanol in the presence of NaCl 200 g/L, then washed with ethanol/water mixture from 70 to 100% v/v in ethanol, and dried at 30°C under vacuum for 48 h. In all cases the xanthan weight recovered was equal at least to 80% of the initial xanthan in solution. Since most of the xanthan is precipitated, these samples recovered are representative in each case of the xanthan after aging.

The weight-average molecular weight, M_w , was measured with a low-angle laser light scattering photometer (Chromatix KMX 6 U.S.A.) at 0.1 g/L xanthan concentration using 0.01M NaCl as the solvent. Clarification of xanthan solutions was done by filtration through 0.22 μm Millipore filters (type GS). We have not checked the xanthan concentration after filtration, but the solution viscosity before and after filtration was usually the same. The specific refractive index increment was determined at λ = 546 nm using a Brice-Phoenix differential refractometer without dialysis. The value of dn/dc obtained was 0.155 mL/g in 0.01M NaCl.

The viscosity measurements were carried out either directly on the test solution (Table I), or at 1 g/L xanthan concentration using 0.01M NaCl as the solvent (Table II) with a low-shear LS 30 Contraves viscometer equipped with a Haake thermostat.

Proton NMR measurements were performed at 85°C on a Brüker WP 100 MHz spectrometer with suppression of the OH signal by irradiation. Two hundred scans were accumulated with a repetition time of 7 s and a sweep

TABLE I
Xanthan Properties as a Function of Storage Time^a

| Experiment | t°C | Sparge | Bactericide | O ₂ (scavenger) | Storage (mon) | O ₂ (ppb) | pH | η (cP), 30°C, $\dot{\gamma} = 7 \text{ s}^{-1}$ | Acetyl | Pyruvate |
|------------|-----|-----------------|--|---|------------------|----------------------|-----|---|--------|----------|
| 0 | 80 | — | — | — | 0 | > 1000 | 7.0 | 53 | 0.7 | 0.22 |
| 1 | 80 | CO ₂ | — | — | 2 | > 1000 | 4.7 | 3.5 | 0 | 0 |
| | | | | | 0 | 80 | 4.1 | 51.3 | 0.71 | 0.25 |
| | | | | | 2 | 5 | 3.8 | 10.5 | 0 | 0 |
| 2 | 80 | CO ₂ | — | N ₂ H ₄ , 1000 ppm | 6 | 10 | 3.9 | 3 | 0 | 0 |
| | | | | | 0 | 50 | 5.9 | 52.5 | 0.22 | 0.16 |
| | | | | | 2 | 10 | 5.9 | 30 | 0 | 0.21 |
| 3 | 80 | — | — | Na ₂ SO ₃ , 1000 ppm | 6 | 10 | 5.8 | 28 | 0 | 0.11 |
| | | | | | 0 | 25 | 9.7 | 45 | 0 | 0.21 |
| | | | | | 2 | 5 | 7.9 | 26 | 0 | 0.22 |
| 4 | 80 | CO ₂ | 2-butanol, 6000 ppm, 2,4,6,T, 200 ppm | — | 6 | 5 | 7.7 | 22.3 | 0 | 0.24 |
| | | | | | 0 | 300 | 4.6 | 52.5 | 0.64 | 0.12 |
| | | | | | 2 | 60 | 4.7 | 8.3 | 0 | 0 |
| | | | | | 6 | 40 | 4.4 | 14 | 0 | 0 |
| 5 | 60 | CO ₂ | Formaldehyde, 500 ppm, 2,4,6,T, 200 ppm | Na ₂ SO ₃ , 1000 ppm | 0 | 80 | 5.4 | 51 | 0.7 | 0.22 |
| | | | | | 2 | 40 | 5.5 | 35.7 | 0.14 | 0.27 |
| | | | | | 6 | 40 | 5.4 | 31 | — | — |
| 6 | 40 | — | Formaldehyde, 500 ppm | — | 0 | > 1000 | 7.0 | 53 | 0.7 | 0.22 |
| | | | | | 2 | > 1000 | 4.3 | 50.5 | 0.55 | 0.22 |
| | | | | | 6 | > 1000 | 3.9 | 46 | — | — |

^a Brine composition: NaCl, 100 g/L; CaCl₂, 10 g/L; MgCl₂, 10 g/L except experiment 3: NaCl, 100 g/L.

TABLE II
Xanthan Characterizations in 0.01M NaCl as a Function of Storage Time

| Experiment | t (°C) | Spurge | Bactericide | O ₂ (scavenger) | Storage (mon) | O ₂ (ppb) | pH | η (cP), 25°C, $\dot{\gamma} = 7 \text{ s}^{-1}$ | | $\bar{M}_w \times 10^6$ | |
|------------|--------|-----------------|--|---|------------------|----------------------|-----|---|------|-------------------------|------|
| | | | | | | | | a | b | a | b |
| 0 | 80 | — | — | — | 0 | > 1000 | 7.0 | 45 | 16 | 2.2 | 1.5 |
| 1 | 80 | CO ₂ | — | — | 2 | 5 | 3.8 | — | 2 | — | 0.7 |
| 2 | 80 | CO ₂ | — | N ₂ H ₄ 1000 ppm | 2 | 10 | 5.9 | — | 16 | 2.2 | — |
| 3 | 80 | — | — | Na ₂ SO ₃ , 1000 ppm | 0 | 25 | 5.8 | 28 | 3 | 2.0 | — |
| | | | | | 2 | 5 | 9.7 | 35 | 16.2 | 2.26 | 1.5 |
| 4 | 80 | CO ₂ | 2-Butanol, 6000 ppm, 2,4,6,T, 200 ppm | — | 6 | 5 | 7.9 | 23 | 8 | 2.4 | 0.7 |
| | | | | | 0 | 300 | 4.6 | 48 | — | 3.1 | — |
| 5 | 60 | CO ₂ | Formaldehyde, 500 ppm, 2,4,6,T, 200 ppm | Na ₂ SO ₃ , 1000 ppm | 2 | 60 | 4.7 | 8.5 | 1.5 | 1.17 | 0.44 |
| | | | | | 2 | 40 | 5.5 | 32 | 4.4 | 1.9 | 1.0 |
| 6 | 40 | — | Formaldehyde, 500 ppm | — | 2 | > 1000 | 4.3 | 41 | 7.2 | 2.6 | 1.2 |

^a Measurements made directly on 1 g/L xanthan in 0.01M NaCl that was obtained after precipitation.

^b As above, but with heating 1 min at 80°C.

width of 1125 Hz. Dried xanthan was dissolved in 0.005*M* sodium acetate D₂O solution at a polymer concentration equal to about 5 g/L. The acetyl and pyruvate substituent contents were determined by measuring the peak areas of the acetate ($\delta = 2.09$ ppm) and pyruvate ($\delta = 1.4$ ppm) in comparison with sodium acetate ($\delta = 1.8$ ppm). Chemical shifts were referenced to Me₄Si. Depending on the solubility of the precipitated xanthan, the accuracy of the NMR method, usually equal to ± 0.05 substituents per side chain can be larger.

RESULTS AND DISCUSSION

Substituent Contents

As shown in Table I, the initial xanthan contains about 0.7 acetyl groups per side chain. After 2 months aging, all the acetyl groups were hydrolyzed even in acid medium. In basic medium hydrolysis was already complete immediately after sample preparation (experiment 3), or partially hydrolyzed as for experiment 2 where the pH was higher than 7 at the time of N₂H₄ addition, and went down to 5.9 during CO₂ stripping.

Initially about 0.25 side chains contain a pyruvate group. Sample preparation did not modify this content except perhaps for experiment 4. (The solutions of experiment 4 were not clear and, as a result, the substituent content results were not certain.) The pH and the temperature were the only parameters which influenced the pyruvate hydrolysis. At 80°C when the pH was lower than 5.5 all the pyruvate groups were hydrolyzed after 2 months. For pH higher than 5.5 we found pyruvates even after 6 months at 80°C. The presence of the pyruvate after 6 months shows that the side chains are not hydrolyzed at least in these cases.

Viscosities and Molecular Weights

Comparison of the viscosities given in Table I shows that conditions 2 and 3 indicate relatively good thermal stability. Because the precise xanthan concentration of the initial diluted broth is not known, and the nature and concentration of the external salts are not the same for all experiments, xanthan samples were precipitated in order to obtain reliable \bar{M}_w and η values. \bar{M}_w and η were measured after redissolution. However, we have shown previously¹⁶⁻¹⁸ that masked breaks in the main chain can remain after partial degradation of the xanthan. These breaks are stabilized by noncovalent interactions in the ordered xanthan conformation. The destabilization of these breaks is obtained during the denaturation of the ordered conformation and leads to a separation of different parts of the main chain. To test this behavior, the samples precipitated were dissolved at 1 g/L xanthan concentration in 0.01*M* NaCl. \bar{M}_w and η values were measured directly from these solutions (condition a) and after having heated these solutions 1 min at 80°C (condition b). (Condition b can also be obtained by dissolving xanthan in water and adding 0.01*M* NaCl just before measurements.) Condition a corresponds to xanthan, possibly containing masked breaks, while condition b corresponds to a form which has been disordered and then restored to

conditions favoring order. By doing so, any masked breaks are removed and a net decrease in apparent molecular weight and viscosity is observed (see Table II). We can notice that, by comparing η and \bar{M}_w values (a and b) for experiment 0 at $t = 0$, masked breaks already exist in the initial xanthan broth. After 2 or 6 months these masked breaks increase in all cases. For experiment 3 at $t = 2$ months there is an average of about two breaks per xanthan chain. In addition, we have noticed during this work that after storage of the xanthan powder several months at ambient conditions, the \bar{M}_w found are larger than the ones measured several days after precipitation of the xanthan whereas the viscosities remain about the same. This behavior is contrary to our finding for the masked breaks where η and \bar{M}_w changed simultaneously. We assume that intermolecular associations may appear in the solid state during storage, which could explain the inconsistencies of several \bar{M}_w values, particularly in condition a.

From this work, three parameters seem to be important in controlling xanthan viscosity stability: temperature, oxygen concentration (a decrease in oxygen concentration by sparging with oxygen free gas or using O_2 -scavenger additives enhances thermal stability), and pH (at comparable oxygen concentrations, the pH influences stability, thus the best results are obtained for pH values higher than 5.5).

Our results are in agreement with those of Wellington¹⁵ using different additives. Nevertheless, basic solutions are incompatible with tertiary oil recovery because precipitation can occur. Therefore, the results most suited to tertiary oil recovery are typified by experiment 2 where we have stabilized the loss of solution viscosity at 50% of its initial value. The major part of this loss takes place during the first 2 months. The important point here is that the xanthan solution has never passed through disordering conditions. As shown in Table II even a brief exposure to such conditions as heating in 0.01M NaCl for 1 min at 80°C and cooling is sufficient to cause a dramatic additional viscosity loss. Thus 6 months aging caused less than 50% viscosity loss while one brief cycle from the ordered to disordered form and back, caused a further reduction to 7% of the initial value.

CONCLUSION

We show the importance of oxygen concentration, pH, and temperature on the stability of xanthan during aging. In each case (Table I), the acetyl groups were hydrolyzed. In the absence of buffer this hydrolysis lead to a decrease in pH and concomitant pyruvate hydrolysis and acidic degradation of the polymer chain. In neutral or basic conditions the pyruvate groups were quite stable and in very low oxygen concentration levels the viscosity level of xanthan solution was stabilized to about 50% of its initial value after 6 months at 80°C. However, this conclusion is valid as long as the xanthan remains in its ordered conformation; otherwise an additional loss in viscosity and molecular weight appears. The assumption is made that masked breaks in the main chain were formed when the degradation takes place when xanthan is ordered.

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