

Nonaqueous Fluid Xanthation of Alkali Cellulose

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Introduction

Commercially, xanthation of alkali cellulose is carried out as a solid-gas reaction. Liquid carbon disulfide is mixed with the alkali cellulose but the greatest part of the reaction results from the vaporization of the carbon disulfide and its subsequent gaseous diffusion throughout the mass. Operational problems arise in this system principally as the result of poor initial mixing of the very large volume of fluffy alkali cellulose with a relatively small volume of carbon disulfide. Either agitation or addition of the carbon disulfide in portions rather than all at once is required to produce an easily dissolved xanthate. Temperature control is very critical, for elevated temperature (above 35°C.) generally displaces the reaction toward by-product formation.

Process Description

A method for preparing an especially uniform mixture of alkali cellulose and carbon disulfide was conceived as a process that would employ a fluidizing medium miscible with carbon disulfide. The fluidizing liquid was chosen to be immiscible with water and a nonsolvent for sodium hydroxide, alkali cellulose, cellulose xanthate, and the various other components of viscose. Straight-chain hydrocarbons, such as *n*-hexane and *n*-heptane, satisfy these requirements.

A nonaqueous fluid xanthation process would comprise a slurring stage wherein the alkali cellulose and carbon disulfide are reacted in enough of the selected organic liquid to provide an easily stirred mixture.

The slurring stage would be followed by a filtering step to separate the xanthate and then a mixing stage to convert the xanthate into viscose. There would also be a solvent recovery system to reclaim and reuse the organic liquid.

Laboratory Evaluation and Results

Such a process was simulated in the laboratory and found to overcome more than adequately the previous difficulties associated with poor carbon disulfide distribution. Since the carbon disulfide is completely miscible with the organic fluid used to slurry the alkali cellulose, there is extreme uniformity of contact of these two reactants. Additionally, since the organic liquid is not miscible with water or a solvent for sodium hydroxide, the alkali cellulose and xanthation reaction sites are at a high alkalinity (14%) to promote reaction. There is no problem with mixture viscosity, for there is no limit to the amount of fluidizing agent that can be used.

For this system the reaction rate is proportional to the concentration of carbon disulfide and to the temperature. To produce a xanthate of the desired degree of substitution in a time comparable to plant performance requires approximately the same ratio of carbon disulfide to reactants (alkali cellulose plus organic) as is now used when no organic liquid is present. The system then must contain a large excess of carbon disulfide to promote reaction, but this can be recycled with the organic liquid with only the amount actually used added as make-up. Refractive index was used to measure the percentage of carbon disulfide in the fluidizing agent. Figure 1 is a representation of the reaction rate versus carbon disulfide concentration at about 30°C.

In addition to the primary purpose of xanthating alkali cellulose several unusual results were observed, all of which can be attributed to the near perfect distribution of the reactants.

Filterable viscoses (this is the prime criterion used commercially to evaluate viscose quality) with very low xanthate sulfur contents were produced. In conventional processes the particles of alkali cellulose are contacted by varying amounts

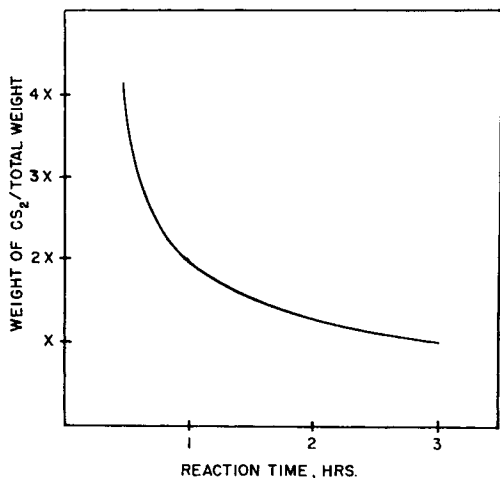


Fig. 1. Xanthation time as a function of carbon disulfide concentration (constant temperature).

of carbon disulfide and therefore some become overxanthated while others are underxanthated. We must aim for a higher than necessary xanthate level, so that the lower xanthated fraction is reacted sufficiently to dissolve in the water-caustic mixer make-up.

With these low xanthate contents it is possible to bypass the ripening operation and cast the viscose immediately after mixing and deaeration.

Viscose of identical composition (both xanthate and by-product sulfur percentages) can be produced at widely different processing condition. Again in Figure 1 relating reaction time to carbon di-

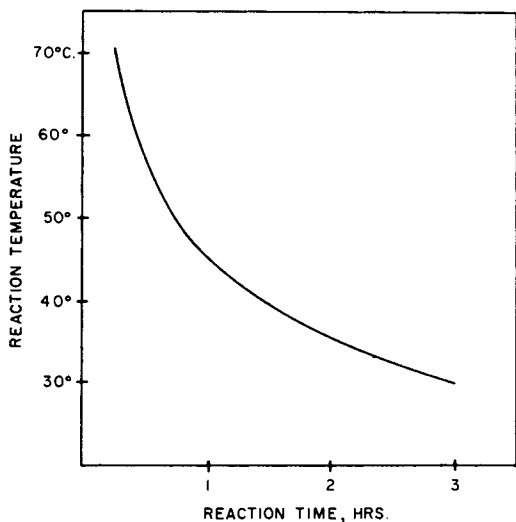


Fig. 2. Reaction time as a function of reaction temperature (constant CS₂ concentration).

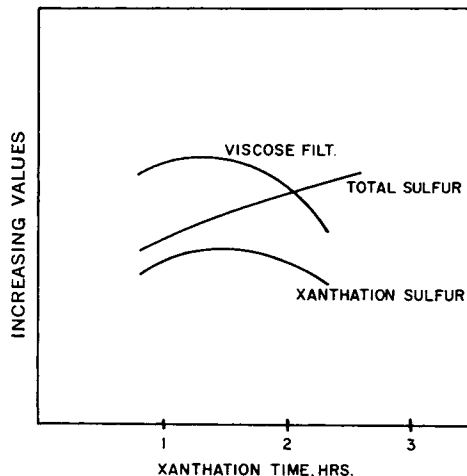


Fig. 3. The effect of reaction time on sulfur content and viscose filterability (constant temperature).

sulfide concentration, the points shown have the same by-product concentrations as well as xanthate degree of substitution. The viscose filterabilities of the viscose solution (grams to plug) are also nearly equal under the several conditions.

The effect of reaction temperature upon the reaction rate is shown in Figure 2. A 10°C. increase in temperature approximately doubles the reaction rate. Again, the products were identical under the several processing conditions.

The ability to produce equivalent composition viscoses under widely differing process conditions seems to be unique to this method of xanthation. In the commercial solid-gas reactors an increase in temperature will increase the rate of by-product sulfur formation more than it increases the rate of xanthation. We therefore are unable to increase throughput merely with higher temperatures and shorter reaction times, as the products differ in composition.

In this nonaqueous system it was found that when the reaction times were extended to much longer than is needed, xanthate sulfur content reaches a maximum and then decreases. Viscose filterability parallels this, in that it also peaks at about the maximum xanthate level. However, the filterability decreases far more rapidly than does the xanthate content. Total sulfur increases throughout the entire period (Fig. 3).

The xanthate prepared by this system is more easily dispersed than is the xanthate prepared in conventional processes. Commercial xanthate requires a mild alkaline mixer solution if it is to

dissolve properly. If only water is used, dissolution is extremely difficult because of the formation of many lumps or balls of xanthate, and even after these are dispersed the viscose has a very low filterability. The nonaqueous variety of xanthate will readily dissolve in water with no particular tendency to form balls. The resulting viscose is of lower filterability than if an alkaline solution were used, but its level is still acceptable to commercial use.

Commercially, a process for nonaqueous xanthation would require a mixing operation to react the carbon disulfide and alkali cellulose in the organic fluidizing medium followed by filtration of the xanthate. The xanthate must then be dissolved to produce viscose. A solvent-recovery system is required to recirculate the fluidizing agent. It is this latter aspect which makes the process unattractive economically.

The majority of the efforts in this work have been directed toward a possible commercialization of an organic fluid xanthation system. However, it is possible by selecting liquids other than the straight-chain hydrocarbons to obtain unusual products that are of interest in the laboratory. The chlorinated hydrocarbons and cyclic hydrocarbons and acetone exhibit tendencies to dissolve the by-product sulfur, leaving the xanthate in suspension. After completion of the reaction, we can thereby filter off a by-product free xanthate for evaluation or conversion to viscose. The by-product sulfur is more soluble in acetone than in the chlorinated solvents, and, by using different liquids, products of varying ratios of xanthate to by-product can be produced.

Synopsis

Xanthation can be accomplished by slurring the alkali cellulose in an organic liquid chosen to be miscible with carbon disulfide, immiscible with water, and a nonsolvent for sodium hydroxide, alkali cellulose, cellulose xanthate, and other components of viscose. Straight-chain hydrocarbons, such as *n*-hexane and *n*-heptane, satisfy these requirements and function very well. A viscose preparation system using this method of xanthation would consist of a slurry step wherein the alkali cellulose and carbon disulfide are reacted in the selected organic liquid, a filtering step to remove the xanthate from the liquid, and a mixing operation to dissolve

the xanthate in weak alkali to produce viscose. Because of the near-perfect distribution of carbon disulfide throughout the reaction, this method of xanthation produces filterable viscoses at very low degree of substitution. It is also possible to produce viscose of identical composition at widely different process conditions by various combinations of temperature, reaction time, and carbon disulfide concentration.

Résumé

La xanthation peut être réalisée en coulant l'alkali cellulose dans un liquide organique miscible au sulfure de carbone, insoluble dans l'eau et un non-solvant pour l'hydroxyde de soude, l'alkali cellulose, le xanthate de cellulose et les autres constituants de la viscose. Des hydrocarbures à chaîne linéaire comme le *n*-hexane et le *n*-heptane satisfont à ces exigences et conviennent très bien. Une préparation de viscose utilisant cette méthode de xanthation consisterait en une étape lente où l'alkali cellulose et le sulfure de carbone réagiraient dans un liquide organique adéquat, en une étape de filtration pour récupérer le xanthate de la solution et une étape pour dissoudre le xanthate dans un alkali faible pour produire la viscose. En raison de l'excellente répartition du sulfure de carbone tout au long de la réaction, cette méthode de xanthation produit des viscoses filtrables à de très bas degrés de substitution. Il est aussi possible de produire des viscoses de composition identique dans des conditions très différentes en faisant varier les conditions de température, la durée de réaction et la concentration en sulfure de carbone.

Zusammenfassung

Xanthogenierung kann durch Bildung einer Aufschlammung von Alkalicellulose in einer mit Schwefelkohlenstoff mischbaren und mit Wasser nichtmischbaren organischen Flüssigkeit erreicht werden, in welcher Natriumhydroxyd, Alkalicellulose, Cellulosexanthogenat und andere Viskosekomponenten nicht löslich sind. Offenkettige Kohlenwasserstoffe wie *n*-Hexan und *n*-Heptan genügen dieser Bedingung und können gut verwendet werden. Eine Viskoseherstellung nach dieser Xanthogenierungsmethode würde aus dem Aufschlammvorgang, bei welchem die Alkalicellulose und Schwefelkohlenstoff in der ausgewählten organischen Flüssigkeit zur Reaktion gebracht werden, der Filtration zur Abtrennung des Xanthogenates von der Flüssigkeit und dem Mischungsvorgang zur Lösung des Xanthogenates in schwachem Alkali unter Bildung von Viskose bestehen. Wegen der nahezu vollkommenen Verteilung des Schwefelkohlenstoffes während der Reaktion liefert diese Xanthogenierungsmethode filtrierbare Viskosen bei sehr niedrigem Substitutionsgrad. Ausserdem ist es möglich bei sehr verschiedenen Versuchsbedingungen durch geeignete Kombination von Temperatur, Reaktionsdauer und Schwefelkohlenstoffkonzentration Viskose von gleicher Zusammensetzung herzustellen.