

## UNITED STATES PATENT OFFICE

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## SHORT STOP XANTHATION

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1 Claim. (Cl. 260—216)

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This invention relates to an improved process for xanthating alkali cellulose.

Many attempts have been made to shorten xanthation time and thereby increase throughput of xanthating vessels. Attempts to speed up xanthation at normal operation temperatures either have not been successful at all or, if the time cycle was reduced, non-uniform or incomplete reaction of the alkali cellulose with the carbon bisulfide resulted in such low quality viscose as not to be useful. It is, of course, generally known that when xanthation is carried out at more elevated temperature than normally used that the reaction can be speeded up but invariably there has been a corresponding loss in quality as measured by filterability of the viscose solution made therefrom.

It is, therefore, an object of this invention to provide a short time xanthation cycle, using standard equipment, without sacrificing the quality of the cellulose xanthate and, in fact, to improve it. Other objects will appear from the following description and claim.

The objects of the present invention are accomplished by a process which comprises charging a conventional baratte with alkali cellulose crumbs, xanthating the alkali cellulose at an elevated temperature with a substantial excess of carbon bisulfide over the amount actually absorbed by the alkali cellulose, and stopping the reaction short of completion by removing the excess carbon bisulfide from the baratte when the desired amount of carbon bisulfide has been absorbed. This process will be referred to hereafter as short-stop xanthation.

Normal aged alkali cellulose crumbs prepared from any of the usual sources of cellulose are suitable for the process. The baratte is of the conventional rotating type known to those skilled in the art, an illustration of which will be found on page 116 of "Synthetic Fiber Developments in Germany" by Leroy H. Smith (Textile Research Institute, Inc., New York, 1946). Either vacuum xanthation or the alternative method of venting the baratte to the atmosphere may be used with improved results.

The amount of carbon bisulfide added to the baratte should be in the range of from 20% to 150% more than the amount actually absorbed after the desired degree of xanthation substitu-

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tion is reached. The xanthation temperature should be in the approximate range of from 20° to 60° C. and preferably in the range of from 25° to 45° C. With these preferred conditions of 20% to 150% excess carbon bisulfide and a xanthation temperature of 25° to 45° C., the xanthation cycle has been reduced to 25% to 80% of the time required for the conventional xanthation cycle, which uses a temperature of approximately 30° C. and very little excess (approximately 5%) of carbon bisulfide, which is in equilibrium with the reacted xanthate. This reduction in time is accomplished without sacrificing the quality of cellulose xanthate produced. In fact, a surprising improvement in filterability of 30% or more is achieved for the same total and combined sulfur contents.

In short-stop xanthations the alkali cellulose is charged and the baratte prepared for carbon bisulfide addition in the same manner as for conventional xanthation. At this point the two procedures digress. Rather than adding a mere 30% of carbon bisulfide (based on air dry pulp), as is the case for conventional xanthation, an excess of 20% (36% carbon bisulfide on an air dry basis) or more is added to the baratte in the short-stop procedure. The total amount of carbon bisulfide is added in the same time period used for conventional xanthations (approximately 10 minutes). The reaction is allowed to proceed until the desired degree of xanthate substitution is achieved regardless of whether or not all the liquid carbon bisulfide added to the baratte is in the vapor state. At this point the baratte is evacuated as in the conventional procedure. If any liquid carbon bisulfide remains in the baratte at the time of evacuation, it is vaporized and removed at that time. It must be noted that if the xanthation is allowed to proceed until an equilibrium state is reached, as is the case with conventional xanthations, than the xanthate produced will be too highly substituted. This does not mean that the short-stop xanthation procedure is not suitable for the production of highly substituted xanthates. On the contrary, the short-stop procedure is advantageous in this case because decomposition is minimized due to the shortened time cycle which obtains.

Short-stopping in the presence of liquid car-



bon bisulfide is not detrimental but is, in fact, advantageous. This latter state of affairs is rather surprising. One would think that if a xanthation is stopped while liquid carbon bisulfide was still present, even though the liquid was later vaporized and removed, the reaction mixture would be heterogeneous and that a poor filtering viscose would result. This is not the case.

The highly unexpected and desirable results mentioned above are shown by the examples summarized in the tables below. All of these examples were conducted under comparable conditions using the conventional procedure for vacuum xanthation, except as noted in the tables. The percentages of carbon bisulfide added and absorbed are expressed in terms of air dry pulp. The percentages of sulfur were determined immediately after mixing. The values for filterability are the number of grams of viscose passing through a 1/4 square inch area of standard filter press dressing in 60 minutes under a pressure of 60#/sq.in. (gage) at a temperature of 18° C. using a viscose containing 7% cellulose and 6% caustic soda.

TABLE I

Comparison of short-stop with conventional xanthation at 29° and 43° C.

Example.....	1	2	3	4	5
Percent CS <sub>2</sub> Added to Baratte.....	30.0	30.0	39.0	50.0	60.0
Percent CS <sub>2</sub> Absorbed.....	23.2	28.4	28.6	28.2	28.3
Percent Excess CS <sub>2</sub> Used <sup>1</sup> .....	<sup>2</sup> 6.4	<sup>2</sup> 5.6	<sup>3</sup> 36.4	<sup>3</sup> 74.8	<sup>3</sup> 112.0
Xanthation Temp. (°C.).....	30.0	43.0	43.0	43.5	44.0
Xanthation Cycle (Min.).....	90.0	45.0	33.0	28.0	25.0
Percent Reduction in Xanthation Cycle.....	0.0	50.0	63.4	69.0	71.5
Mixer Salt Index.....	9.2	6.5	9.2	9.2	9.5
Percent Total Sulfur in Viscose.....	1.94	1.91	1.98	1.96	1.98
Percent Xanthate Sulfur in Viscose.....	1.34	1.25	1.36	1.37	1.40
Viscose Filterability.....	900	400	900	1,200	1,400
Percent Filterability of Control.....	-----	44.4	100.0	133.3	155.8

Example 1—conventional vacuum Xanthation at 30° C.  
Example 2—conventional vacuum Xanthation at 43° C.  
Examples 3, 4, and 5—43° C.—“short-stop xanthation.”  
 $\text{Percent Excess CS}_2 = \frac{\text{CS}_2 \text{ added} - \text{CS}_2 \text{ absorbed}}{\text{CS}_2 \text{ absorbed}} \times 100$   
<sup>2</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub> vapor remaining in the baratte and at equilibrium with the xanthate at the end of the reduction.  
<sup>3</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub>, vapor or liquid, remaining in the baratte and not at equilibrium with the xanthate when the reaction is short-stopped.

TABLE II

Comparison of short-stop with conventional xanthation at 29° and 34° C.

Example.....	1	2	3	4
Percent CS <sub>2</sub> Added to Baratte.....	25.0	60.0	35.0	50.0
Percent CS <sub>2</sub> Absorbed.....	24.4	23.4	24.2	25.2
Percent Excess CS <sub>2</sub> Used <sup>1</sup> .....	<sup>2</sup> 2.5	<sup>3</sup> 156.2	<sup>3</sup> 44.6	<sup>3</sup> 98.4
Xanthation Temp. (°C.).....	29.0	29.0	34.0	33.0
Xanthation Cycle (Min.).....	90.0	50.0	50.0	40.0
Percent Reduction in Xanthation Cycle.....	0.0	44.4	44.4	55.5
Mixer Salt Index.....	6.8	5.9	6.2	6.5
Percent Total Sulfur in Viscose.....	1.78	1.69	1.76	1.79
Percent Xanthate Sulfur in Viscose.....	1.20	1.15	1.18	1.21
Viscose Filterability.....	750	1,000	1,150	1,300
Percent Filterability of Control.....	-----	133.3	153.2	173.5

Example 1—conventional vacuum xanthations at 29° C.  
Example 2—29° C.—short stop xanthation.  
Examples 3 and 4—34° C.—short stop xanthations.  
 $\text{Percent excess CS}_2 = \frac{\text{CS}_2 \text{ added} - \text{CS}_2 \text{ absorbed}}{\text{CS}_2 \text{ absorbed}} \times 100$   
<sup>2</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub> vapor remaining in the baratte and at equilibrium with the xanthate at the end of the reaction.  
<sup>3</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub>, vapor or liquid, remaining in the baratte and not at equilibrium with the xanthate when the reaction is short-stopped.

TABLE III

Comparison of “short-stop” vented and “short-stop” vacuum xanthation with conventional xanthation at 34° C.

	Type of Xanthation		
	Conventional Vacuum	“Short-Stop” Vented	“Short-Stop” Vacuum
Percent CS <sub>2</sub> Added to Baratte.....	30.0	35.0	<sup>1</sup> 36.0
Percent CS <sub>2</sub> Absorbed.....	28.4	28.4	23.4
Percent Excess CS <sub>2</sub> Used <sup>2</sup> .....	<sup>3</sup> 5.6	<sup>4</sup> 23.3	<sup>4</sup> 26.8
Xanthation Temp. (°C.).....	34.0	34.0	34.0
Xanthation Cycle (Min.).....	75.0	55.0	55.0
Percent Reduction in Xanthation Cycle.....	16.7	38.8	38.8
Mixer Salt Index.....	8.0	9.0	9.3
Percent Total Sulfur in Viscose.....	1.96	1.94	1.96
Percent Xanthate Sulfur in Viscose.....	1.33	1.39	1.38
Viscose Filterability.....	1,200	1,700	1,700
Percent Filterability of Control.....	-----	141.4	141.5

<sup>1</sup> Approximately 1% CS<sub>2</sub> lost through vent during the reaction cycle.  
<sup>2</sup> Percent excess CS<sub>2</sub> =  $\frac{\text{CS}_2 \text{ added} - \text{CS}_2 \text{ absorbed}}{\text{CS}_2 \text{ absorbed}} \times 100$ .  
<sup>3</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub> vapor remaining in the baratte and at equilibrium with the xanthate at the end of the reaction.  
<sup>4</sup> These excesses of CS<sub>2</sub> represent the amount of CS<sub>2</sub>, vapor or liquid, remaining in the baratte and not at equilibrium with the xanthate when the reaction is short-stopped.

Table I is a comparison of a normal vacuum xanthation carried out at 30° C. and one carried out at 43° C. with three short-stop xanthations carried out at 43° C. using various excesses of CS<sub>2</sub>. It can be seen from this data that a shortening of cycle by merely increasing the temperature results in a loss of filterability. (See columns 1 and 2.) The loss in filterability can be restored and even exceeded by using the short-stop technique. (See columns 3, 4, and 5.)

Table II is a comparison of short-stop xanthation with conventional vacuum xanthation at two lower temperatures and at a lower degree of xanthate substitution. It, too, shows the advantages of improved filterability afforded by the short-stop procedure.

Table III is a comparison of a conventional vacuum xanthation with short-stop vented and vacuum xanthations at 34° C. This table shows the equivalency of the vented and vacuum procedures and also shows again the improved filterability for the short-stop xanthations.

By the present invention the time required for the xanthation cycle is markedly reduced and the filterability of the viscose product is materially increased while maintaining other properties of the product, such as total and combined sulfur, in line with the results of conventional process conditions. The throughput of the conventional baratte is thereby greatly increased with a substantial improvement in the quality of product obtained.

As different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific processes disclosed except as defined in the appended claim.

What is claimed is:

In the process of xanthating alkali cellulose crumbs to produce viscose, the improvements for producing viscose of improved filterability which comprises introducing into the charge of alkali cellulose crumbs to be xanthated within a time period of approximately 10 minutes an amount of carbon bisulfide which is from 20% to 150% in excess of the amount to be absorbed by



the alkali cellulose, xanthating by tumbling the alkali cellulose at a temperature in the range of from 25° to 45° C., and stopping the xanthation short of equilibrium by removing the excess carbon bisulfide from the zone of reaction after a xanthation cycle of from 25% to 80% of the time required to reach substantial equilibrium in a conventional xanthation using an amount of carbon bisulfide which is approximately 5% in excess of the amount absorbed and xanthating at a temperature of 30° C.

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The following references are of record in the file of this patent:

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