

1

3,600,379

PROCESS FOR MAKING VISCOSE

Hannes Sihtola, Tiilikari 30 A, and Boris Nizovsky,
Gyldenintie 14 A, both of Helsinki, Finland
No Drawing. Filed May 16, 1969, Ser. No. 825,390
Claims priority, application Finland, May 24, 1968,
1,466/68; July 17, 1968, 2,036/68

Int. Cl. C08b 9/00

U.S. Cl. 260—217

6 Claims

ABSTRACT OF THE DISCLOSURE

Process for manufacturing viscose including the step of re-steeping and pressing aged alkali cellulose with a sodium hydroxide solution, the concentration of which is less than 15% by weight, prior to reacting the alkali cellulose with carbon disulfide. The re-steeping and pressing steps reduce the amount of sodium hydroxide in the aged alkali cellulose. The amount of sodium hydroxide in the alkali cellulose is maintained at less than 15 wt. percent during xanthation, resulting in an aged alkali cellulose which requires a low amount of carbon disulfide to yield a xanthate.

The invention relates to a process for the manufacture of viscose from raw material containing cellulose. It is well known that the preparation of the spinning or casting solution—viscose—in the manufacture of viscose fibers and films is conventionally effected as follows:

(1) The pulp utilized as raw material is steeped either as sheets or slurry with 17–22 percent NaOH solution.

(2) The excess steeping liquor is removed by pressing so that the resulting alkali cellulose contains 30–35 percent cellulose; its NaOH content is then 15–17 percent.

(3) The alkali cellulose is shredded and aged at 20–60° C. until the molecular size of the cellulose is reduced to the desired level. The higher the temperature, the faster is the depolymerization process. The reaction can be accelerated by using oxidizers or catalysts, such as peroxides, ions of cobalt, manganese, and so on.

(4) The aged alkali cellulose is xanthated with an amount of carbon disulfide which is dependent upon the product to be manufactured. The proportions most frequently used are: for staple fibers and film 28–35 percent of the amount of cellulose in the alkali cellulose, for "high wet modulus" type staple fiber considerably more, for polynosic fiber as much as 50–60 percent; for filament yarn 32–40 percent, for rayon cord more than 36 percent.

(5) The xanthate is dissolved in NaOH solution, of which the amount and concentration is chosen in such a way that the prepared solution, the viscose, acquires the desired composition: cellulose 4–10 percent and NaOH 2.5–8 percent, dependent upon the product to be manufactured.

(6) The viscose is ripened and filtered once or several times either during or after ripening, and is spun into fibers or cast into film. One condition of good spinnability is that the filterability of the viscose to be spun is good.

The properties of the final viscose product depend upon a number of different factors. The strength characteristics of the fibers and films are perhaps most influenced by the spinning and casting procedure. A notable factor is also the amount of low-molecular weight carbohydrates in the alkali cellulose to be xanthated, as material of this kind exercises a disturbing effect upon the preparation and spinning of viscose, and also upon many properties of the final product. For this reason, the manufacturer of viscose products would prefer to utilize as raw material pulp which contains a minimum of low-molecular weight material, i.e. pulp of a very high alpha cellulose content. How-

2

ever, the costs of production of pulp of this kind are considerable, and this in turn renders less profitable the manufacture of the viscose product.

Nevertheless, the degree of refinement of the pulp used as raw material has no decisive effect upon the amount of low-molecular weight material in the aged alkali cellulose. In fact, at least one half of the low-molecular weight material of the pulp is removed during the first stages of the viscose process, steeping and pressing. However, on aging of the alkali cellulose, the molecules of alpha cellulose, the main component of the pulp, are split to a suitable level for the spinning and the end product, and at the same time new low-molecular weight material is formed to a marked extent. One suitable means of expressing the amount of such low-molecular weight material is by the solubility in 10 percent NaOH solution (S_{10}). The following example gives an idea of the effect of steeping and aging on the amount of low-molecular weight material in the alkali cellulose.

The original pulp was sulphite pulp from conifer, with an alpha cellulose content of 90.8 percent, viscosity 19 cp., S_{10} 11.1 percent, and steeping loss 6.1 percent.

Alkali cellulose:	S_{10} (percent) ¹
Immediately after steeping and pressing	2.8
Aged 24 hours at 25° C.	5.4
Aged 48 hours at 25° C.	6.6
Aged 72 hours at 25° C.	9.1

¹ Calculated on the weight of the original pulp.

However, the low-molecular weight material of the alkali cellulose is detrimental not only to the properties of the final viscose product, but also interferes with the xanthation of the long-chain alkali cellulose. As far as is known, short-chain carbohydrate material of this kind reacts at a considerably higher rate with carbon disulphide than does long-chain alkali cellulose, and consequently correspondingly less carbon disulphide remains available for the latter material.

In addition to the main reaction, the xanthation of carbohydrates, carbon disulphide is also consumed by side reactions, i.e. by reactions with free NaOH present in the alkali cellulose. It is calculated that under ordinary conditions of xanthation these side reactions generally consume 25–35 percent of the amount of CS_2 added.

The largest raw material costs involved in the manufacture of viscose products are those arising from pulp, carbon disulphide, and sodium hydroxide. Manufacturers of viscose products consider that the ratio between NaOH and cellulose in viscose is one of the most important factors which influence the production cost of viscose products. This partly results from the fact that, in addition to the cost arising from the consumption of NaOH, the consumption of sulphuric acid in spinning is directly proportional to the NaOH content of the viscose. If, in a conventional viscose process, 19 percent steeping liquor is used in the manufacture of viscose which contains 9 percent cellulose, a NaOH content of less than 4.8 percent is unattainable, even if the xanthate is dissolved in pure water. The ratio NaOH/cellulose will then be about 0.53–0.54.

In recent years, industry has in general endeavored to convert various batch processes to continuously operating processes. As a rule, this is connected with a reduction in the reaction times, with a view to obtaining a sufficiently large production capacity with small-size machinery. In most cases, it is practicable to raise the reaction temperature, and in this way to reduce the reaction time. So far, it has proved impossible successfully to convert the viscose process for continuous operation, since raising the xanthation temperature increases the velocity of the

CS₂ consuming side reactions more than that of the main reaction, i.e. the formation of cellulose xanthate. Accordingly, 35° C. can be considered as the maximum temperature in conventional xanthation.

The invention to be presented here is aimed at elimination of the disadvantages mentioned above and is chiefly characterized in that the aged alkali cellulose manufactured by known procedures, before xanthation, is steeped at least once with steeping liquor of a concentration below 15 percent, pressed after each steeping, and, after possible shredding subsequent to these steepings and pressings, is xanthated with an amount of carbon disulphide equal to that normally used in the conventional viscose process for the manufacture of the corresponding product, or less than this, the said xanthation being possibly carried out at a considerably higher temperature, and during a shorter period of time than is normal, and that, on dissolving the said xanthate into viscose by known procedures, the NaOH content of the viscose is adjusted to a level lower than normal when xanthation is effected with a normal amount of carbon disulphide, and to a level normal or less than normal when xanthation is effected with an amount of carbon disulphide which is less than normal, and that the entire viscose process may be carried out as a continuous process.

According to the principle of the invention, the procedure may be as follows. After aging, the alkali cellulose is re-steeped. The concentration of the steeping liquor used may be chosen arbitrarily, but with the final result in view about 10 percent NaOH solution is the most advantageous, as at this concentration the NaOH solution has a maximum dissolving and swelling power. At the same time, there is the advantage gained from the content of free NaOH in the alkali cellulose to be xanthated being lower than that in the conventional viscose process, for which reason also the consumption of carbon disulphide by the side reactions with NaOH is reduced in the xanthation.

After the second steeping-pressing operation, the alkali cellulose is shredded, and can be xanthated with an amount of carbon disulphide which is less than normal. This is practicable because alkali cellulose contains much less low-molecular material and NaOH than is usual, and consequently considerably less carbon disulphide is consumed by the reactions with these compounds than in the ordinary process.

If, before xanthation, the alkali cellulose is re-steeped with 10 percent NaOH solution, the NaOH content of the alkali cellulose to be xanthated is about 11 percent. It has proved that the solubility of the xanthate in this case is extremely good, so that, by using a very dilute dissolving lye a viscose of good filterability may be manufactured, with a NaOH content only slightly exceeding 3 percent when the cellulose content is 9 percent. The ratio of NaOH/cellulose achieved is 0.34-0.35.

As the proportion of the side reactions is much less than usual by reason of the low content of low-molecular weight material and NaOH in the alkali cellulose, the xanthation temperature may be increased above that currently applied, for instance to 50° C., without increasing to an unreasonable extent the proportion of carbon disulphide consumed by the side reactions. The xanthation

time may thus be reduced, say to 20-40 minutes, which facilitates making the entire viscose process continuous.

The viscose process is convertible into a continuous process in such a way that the pulp from which the viscose is made is fed as a continuous flow or web into a series of successive reaction vessels and devices, in each of which one or more of the treatments in the preparation of viscose occurs, and that the material after continuously passing through the equipment will have passed in the correct order through either all or some of the stages of the viscose manufacture.

Some examples of applying the method in accordance with the present invention are presented below.

EXAMPLE 1

Eight similar samples of sulphite pulp from conifer, with an alpha cellulose content of 90.8%, and viscosity of 19 cp., were steeped as sheets at 25° C. in exactly the same way, with 19% NaOH solution, and pressed in such a way that the alkali cellulose contained 30.5% cellulose and 15.7% NaOH. All the samples were aged without shredding of the sheets, 4 samples for 60 hours, and 2 samples for 72 hours at 25° C., and the remaining two samples at 60° C. for 3 hours and 3½ hours, respectively. The first-mentioned 4 samples were xanthated without re-steeping, using 29, 26, 23, and 20% carbon disulphide calculated on the amount of cellulose in the alkali cellulose. All the other samples were re-steeped before xanthation, and 10% NaOH solution was used for this steeping. The second steeping of sample 8 was slurry steeping, whereas in the other cases the second steeping was effected as sheet steeping. After the second steeping, the samples were pressed, so that the composition of the alkali cellulose was 32.2% cellulose and 11.2% NaOH. In the xanthation, carbon disulphide was used as follows: sample 5, 20%, sample 6, 16%, sample 7, 18% and sample 8, 20%. The xanthation was carried out at 25° C. for 150 minutes. After xanthation, the cellulose xanthate was in all cases dissolved at 20° C. in NaOH solution of a concentration and amount so chosen that the resulting viscose contained 9% cellulose and 5% NaOH. A ninth sample of the same pulp was steeped in the same way, except that 0.5 mg./liter cobalt as CoCl₂ was added to the first steeping liquor. The viscose was prepared in exactly the same way as that from samples 5 and 8, except that the aging temperature was 50° C. and the aging time 1 hour. After 18 hours of ripening, the viscosity of the viscoses was determined by the falling ball method familiar in viscose technology, and the filterability was evaluated on the basis of the clogging value, K_w. With the filtering device and the filter material applied in the test, and with a viscose composition of 9% cellulose and 5% NaOH and a viscosity of 40-60 seconds, the filterability can be appraised by means of the following scale:

K_w:

300 or less, excellent filterability
300-500, good filterability
500-800, medium filterability
800 or more, poor filterability

The results have been compiled in Table 1.

TABLE 1

Sample	No. of steepings	Aging		Xanthation			Viscose	
		Temperature, ° C.	Time, hrs.	CS ₂ , percent	Temperature, ° C.	Time, mins.	Viscosity, secs.	Filterability, K _w
1.....	1	25	60	29	25	150	42	250
2.....	1	25	60	26	25	150	45	610
3.....	1	25	60	23	25	150	56	1,220
4.....	1	25	60	20	25	150	89	4,520
5.....	2	25	72	20	25	150	43	240
6.....	2	25	72	16	25	150	54	450
7.....	2	60	3	18	25	150	64	450
8.....	2	60	3½	20	25	150	49	510
9.....	2	50	1	20	25	150	88	530

5 EXAMPLE 2

Seven similar samples of sulphite pulp from birch wood, with an alpha cellulose content of 92.2%, and a viscosity of 19 cp., were steeped as sheets at 25° C. in exactly the same way, with 19% NaOH solution, and pressed in such a way that the alkali cellulose contained 31.4% cellulose and 15.6% NaOH. All the samples were aged without shredding, 5 samples for 48 hours at 25°

6

2 for 60 minutes, samples 3 and 4 for 15 minutes, and pressed as in Example 1. Carbon disulphide was used in the xanthation as follows: sample 1, 28%, sample 2, 18%, sample 3, 24%, and sample 4, 20%. In all cases the xanthation temperature was 50° C., and the xanthation time 25 minutes. The viscose prepared contained 9% cellulose and 5% NaOH. The results have been compiled in Table 3.

TABLE 3

Sample	Aging			Steeping II time, mins.	Xanthation			Viscose	
	Steeping I time, mins.	Temper- ature, ° C.	Time, mins.		CS ₂ , percent	Temper- ature, ° C.	Time, mins.	Viscos- ity, secs.	Filter- ability, K _w
1-----	60	60	180	-----	28	50	25	64	15, 00
2-----	60	60	180	60	18	50	25	68	330
3-----	15	50	80	15	24	50	25	38	280
4-----	15	50	80	15	20	50	25	32	380

C. and 2 samples for 2½ hours at 60° C. Samples 1, 2, and 3 were xanthated without re-steeping, by the use of 28, 24, and 22% CS₂, calculated on the amount of cellulose in the alkali cellulose. All the other samples were re-steeped before xanthation, using 10% NaOH solution. After pressing, the alkali cellulose contained 32.9% cellulose and 11.4% NaOH. In the xanthation, carbon disulphide was used as follows: sample 4, 22%, sample 5, 20%, sample 6, 22%, and sample 7, 20%. In all cases, the xanthation was effected at 25° C. for 150 minutes. The xanthate was in each case dissolved at 20° C. in NaOH solution of a concentration and amount so chosen that the resulting viscose contained 8.8% cellulose and 5% NaOH. After 18 hours of ripening, the viscosity of the viscoses was determined by the falling ball method, and the filterability was evaluated on the basis of the clogging value K_w. The results have been compiled in Table 2.

These results indicate that after a single steeping, viscose of acceptable filterability is unobtainable on xanthation at high temperature, even if a normal amount of carbon disulphide is utilized, whereas after double steeping this is practicable, even when a much smaller amount of carbon disulphide than normal is used. In runs 3 and 4, the total time from the start of the first steeping to the end of xanthation was only 150 minutes. From this the conclusion can be drawn that by making viscose manufacture continuous a considerable production capacity can be obtained even with relatively small-size machinery.

EXAMPLE 4

Four similar samples of the sulphite pulp from conifer mentioned in Example 1 were steeped as sheets at 25° C., with 19% NaOH solution, upon which the sheets were pressed as in Example 1, aged at 25° C. for 72 hours,

TABLE 2

Sample	No. of steepings	Aging		Xanthation			Viscose	
		Temperature, °C.	Time, hrs.	CS ₂ , percent	Temperature, °C.	Time, mins.	Viscosity, secs.	Filterability, K _w
1-----	1	25	48	28	25	150	54	450
2-----	1	25	48	24	25	150	64	1,240
3-----	1	25	48	22	25	150	79	3,170
4-----	2	25	48	22	25	150	88	410
5-----	2	25	48	20	25	150	87	640
6-----	2	60	2½	22	25	150	67	380
7-----	2	60	2½	20	25	150	65	490

EXAMPLE 3

Four similar samples of the sulphite pulp from conifer mentioned in Example 1 were steeped as sheets at 25° C. with 19% NaOH solution, samples 1 and 2 for 60 minutes without addition of catalyst, samples 3 and 4 for 15 minutes with lye containing 0.5 mg./l. cobalt as CoCl_2 . All the samples were pressed as in Example 1. Samples 1 and 2 were aged at 60° C. for 3 hours, samples 3 and 4 at 50° C. for 80 minutes, samples 2, 3, and 4 were then steeped with 10% NaOH solution, sample

steeped with 10% NaOH solution, and pressed as in Example 1. All the samples were xanthated with 24% carbon disulphide at 25° C. for 150 minutes. The xanthates were dissolved in such an amount of NaOH solution or water to give a cellulose content of 8.7–8.8% in the viscose. The concentrations of the NaOH solutions were so chosen that the NaOH content of the viscose in sample 1 was 5.0%, in sample 2, 4.0%, and in sample 3 3.5%. The xanthate in sample 4 was dissolved in water. The results have been compiled in Table 4.

TABLE 4

Sample	No. of steepings	Aging		Xanthation			Viscose		
		Temperature, ° C.	Time, hrs.	CS ₂ , percent	Temperature, ° C.	Time, mins.	NaOH, percent	Viscosity, secs.	Filterability, K _w
1-----	2	25	72	24	25	150	5.0	40	110
2-----	2	25	72	24	25	150	4.0	60	230
3-----	2	25	72	24	25	160	3.5	70	190
4-----	2	25	72	24	25	160	3.1	90	450

7 EXAMPLE 5

Eight similar samples of the sulphite pulp from conifer mentioned in Example 1 were steeped as sheets at 25° C., with 19% NaOH solution, and pressed as in Example 1. Samples 1-4 were aged at 60° C. for 3 hours, and samples 5-8 for 3½ hours. All the samples were then steeped with 10% NaOH solution, and pressed as in Example 1. On xanthation, 28% carbon disulphide was used in runs 1, 4, and 7, 24% carbon disulphide in runs 2, 5, and 8, and 20% carbon disulphide in runs 3 and 6. The xanthates were dissolved in NaOH solution of such concentrations that the NaOH content of the viscoses was 5.0% in runs 1-3, 4.0% in runs 4-6, and 3.5% in runs 7-8. The amount of dissolving lye was such that the cellulose content of all viscoses was 8.7-8.8%.

The results have been compiled in Table 5.

TABLE 5

Sample	No. of steepings	Aging		Xanthation			Viscose		
		Temperature, ° C.	Time, hrs.	CS ₂ , percent	Temperature, ° C.	Time, mins.	NaOH, percent	Viscosity, secs.	Filterability, K _w
1-----	2	60	3	28	25	150	5.0	64	260
2-----	2	60	3	24	25	150	5.0	69	220
3-----	2	60	3	20	25	150	5.0	69	450
4-----	2	60	3	28	25	150	4.0	92	230
5-----	2	60	3½	24	25	150	4.0	69	300
6-----	2	60	3½	20	25	150	4.0	65	490
7-----	2	60	3½	28	25	150	3.5	78	270
8-----	2	60	3½	24	25	150	5.5	88	540

The results in Examples 4 and 5 indicate that a second steeping, carried out with 10% NaOH before xanthation, offers a means of preparing, with amounts of CS₂ which are normal or less than normal, viscoses which have a high cellulose content and good filterability, but a NaOH content which is 20-40% lower than normal.

The invention is not restricted to the above working examples, but is variable within the scope of the patent claims. For instance, according to the invention the alkali cellulose can be re-steeped twice or several times in accordance with the object in view, without deviating from the main principle of the invention.

What we claim is:

1. In a process for the manufacture of viscose which includes the steps of steeping a cellulose containing raw material with sodium hydroxide, pressing the resulting alkali cellulose to remove excess sodium hydroxide to produce a first alkali cellulose having at least 15% NaOH by weight based on the weight of said first alkali cellulose, and xanthating the alkali cellulose with carbon disulfide to produce a cellulose xanthate, wherein the improvement comprises resteeeping the aged first alkali cellulose with less than 15% by weight sodium hydroxide solution and thereafter pressing the alkali cellulose, said resteeeping and pressing steps reducing the sodium hydroxide content to produce a second alkali cellulose having a NaOH content of less than 15 weight percent based on the weight of the second alkali cellulose without affecting substantially the weight percent of cellulose present in the second alkali cellulose from the value present in the first alkali cellulose and thereafter xanthating said second alkali cellulose with carbon disulfide, the amount of carbon disulfide being

8

28% or less of the total weight of the cellulose in the second alkali cellulose.

2. The process as set forth in claim 1 also including the step of shredding said alkali cellulose after resteeeping and pressing.

3. The process as set forth in claim 1 wherein the concentration of said sodium hydroxide in said resteeeping step is 10% by weight.

4. The process as set forth in claim 1 wherein the concentration of the carbon disulfide used in the xanthating step is between the range of 16-28% by weight.

5. The process as set forth in claim 1 wherein said xanthation is carried out at a temperature between the range of 35-60° C.

6. A continuous process for the manufacture of viscose comprising the steps of:

- continuously flowing a quantity of aged alkali cellulose into a reaction zone,
- resteeeping said aged alkali cellulose with a less than 15% by weight solution of sodium hydroxide by introducing said sodium hydroxide solution into the reaction zone,
- thereafter pressing the alkali cellulose, said resteeeping and pressing step reducing the amount of sodium hydroxide to less than 15 weight percent based on the alkali cellulose without substantially affecting the cellulose content, and
- thereafter xanthating the resulting alkali cellulose with carbon disulfide, the total amount of carbon disulfide being 28% or less of the total weight of the cellulose in the resulting alkali cellulose.

References Cited

UNITED STATES PATENTS

2,744,292	5/1956	Schlosser et al.	106—164
2,845,416	7/1958	Elling	106—198
2,985,647	5/1961	Kohorn	106—165
3,298,844	1/1967	Swakon	106—165

FOREIGN PATENTS

369,912	3/1932	Great Britain	260—217
---------	--------	---------------	---------

DONALD E. CZAJA, Primary Examiner

60 R. W. GRIFFIN, Assistant Examiner

U.S. Cl. X.R.

106—164, 165

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,600,379 Dated August 17, 1971

Inventor(s) Hannes Sihtola and Boris Nizovsky

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 3, "Fiilimaki" should read --Tiilimaki--.
Column 2, line 71, "viscouse" should read --viscose--;
same line, "containuous" should read --continuous--.
Column 3, line 53, "silghtly" should read --slightly--.
Column 4, line 17, "viscosity" should read --a viscosity--.
Column 5, line 4, "19" should read --18--;
line 63, "minutes, samples" should read --minutes.
Samples--.
Column 6, line 4, "samle" should read --sample--;
Table 3, the heading of column 2 should read
--Steeping I
time,
mins.--;
Table 3, the heading of column 5 should read
--Steeping II
time,
mins.--;
Table 3, column 5, line 1, "-----" should read
-- - --;
Table 3, column 10, line 1, "15,00" should read
--15,000--;
line 62, "3 3.5%" should read --3, 3.5%--.
Column 7, Table 5, column 8, line 8, "5.5" should read
--3.5--;
Table 5, column 9, line 8, "88" should read --78--.
Column 8, lines 9 and 10, "concentration" should read
--amount--.

Signed and sealed this 11th day of April 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents