Patented Feb. 20, 1951 2,542,285

UNITED STATES PATENT OFFICE

2,542,285

CELLULOSE PRODUCTS

Reid Logan Mitchell, Shelton, Wash., assignor to Rayonier Incorporated, Shelton, Wash., a corporation of Delaware

No Drawing. Application July 23, 1946, Serial No. 685,789

7 Claims. (Cl. 260—217)

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This invention relates to purified cellulose especially suitable for conversion into viscose, particularly into viscose of high cellulose and low alkali content. The invention provides an improved cellulose product and an improved method of producing a cellulose product, characterized by low aging requirements which will produce viscose of good filterability. The invention pertains to the production of refined cellulose, such as refined wood pulp, refined cotton, or equivalent forms of cellulose, with a predetermined amount of manganese.

In the production of viscose from ordinary refined cellulose pulps, the cellulose must be appreciably degraded during "aging" of alkali cellulose in order to provide a viscose with low enough viscosity so as to be filtered and spun in the customary manner. Depolymerization is accomplished in the aging process through the oxidizing action of oxygen in the air.

In the manufacture, for example, of cellophane and rayon staple fiber, matters of economy make it desirable to use a viscose with a high content of cellulose and low content of alkali. These conditions greatly increase viscose viscosity and in turn increase the aging requirements needed to obtain the normal level of viscosity.

Since high aging temperatures, as sometimes used, require the installation of expensive continuous and automatic equipment for handling the alkali cellulose, the aging problem has generally been met by producing so-called "low-viscosity" pulps which have been degraded to more than the normal extent in the pulping operations of cooking and bleaching and therefore have lower aging requirements.

There still exists, however, an appreciable gap between the degree of polymerization (D. P.) of pulps as produced and the D. P. normally found in viscose solutions and this gap is being widened with each further reduction in viscose alkalinity, increase in viscose cellulose content, or decrease in carbon disulfide used in xanthation. Furthermore, it becomes increasingly difficult to continue to reduce pulp viscosity by drastic cooking or by heavy bleaching or by a combination of drastic cooking or bleaching without causing undesirable reduction in yield, quality and processing performance, since unduly heavy hydrolysis or bleaching results in much fiber breakdown and

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produces cellulose of relatively non-uniform chain length.

I have discovered that manganese added to refined cellulose as a water soluble manganese compound will not only act effectively in reducing the aging requirements but does so with notable advantages in quality and economy. Hereinafter, for convenience, I shall refer to the addition of manganese as an element and to amounts of manganese preferably as parts per million (P. P. M.) based on the bone dry weight of the cellulose, the actual amounts of the manganese compound added being determined by calculation. The addition of manganese to cellulose results in phenomenal viscosity lowering in subsequent viscose processing, arising from its ability to accelerate the alkaline oxidation of cellulose. Aging of alkali cellulose is probably the best method of accomplishing depolymerization while still maintaining a desirable uniformity in chain length; the cleavage being appreciably more uniform than that resulting from unduly heavy hydrolysis or bleaching. The use of manganese treated cellulose avoids heavy bleaching and permits, for the same aging requirement, the use of a higher viscosity cellulose with attendant advantages in yield or quality and with savings in bleach consumption; or it permits the use of a "low-viscosity" cellulose in the manufacture of very high-cellulose low-alkalinity viscose; or it permits a much reduced aging cycle. I, furthermore, have discovered that cellulose treated with suitable small quantities of manganese shows very good performance in viscose processing and gives markedly reduced aging requirements with no sacrifice in uniformity of viscosity or in viscose filtration. See Table I.

In view of the bad reputation attributed by the viscose industry to "natural" manganese impurities, it was surprising to find that manganese in a selected amount ranging between 1 to 100 P. P. M. could be continuously introduced into the viscose process without causing disastrous loss of viscosity control, and serious drop in viscose filtration. In commercial viscose production there have been many instances in which extremely serious operating difficulties have occurred due to viscose viscosity variations arising (knowingly or not) from manganese in pulp, steeping liquor, or both, and it has been the ac-

cepted practice of pulp, caustic soda, and viscose manufacturers to keep "natural' manganese impurities at as low value as possible and for the sake of uniformity to keep it as much as possible out of the viscose system.

In accordance with my invention, I overcome the undesirable and unpredictable effect of manganese in cellulose by providing a product having uniform quantities of manganese which give desirable results effecting aging of viscose produced therefrom. I provide a cellulose product containing manganese added in an amount varying from 1 to 100 P. P. M. Refined cellulose, such as refined pulp, contains manganese in amounts varying from one-tenth P. P. M. up to four P. P. M. I add a sufficient amount of manganese to raise the manganese to from around 1 P. P. M. to 100 P. P. M. I have found it advantageous to add the manganese in amounts varying from 4 to 20 P. P. M. giving a preferred total amount of manganese varying from around 4 to 25 P. P. M.

If manganese is to be used in the alkali cellulose system there is a tremendous advantage, one might say an essential advantage, to be gained by introducing it in the raw cellulose— namely that of uniformity. Since manganese is very tenaciously adsorbed and stripped from caustic soda steeping liquor by cellulose, it is practically impossible in commercial operation to satisfactorily control the amount of manganese in the steeped alkali cellulose by dissolving manganese salts in the steping liquor effective though they may be in lowering viscosity. The important thing is not merely to lower viscosity but to lower it in a continually uniform manner.

The following examples illustrate methods carried out in accordance with the invention in the preparation of viscose from refined wood pulp.

EXAMPLE I

A web of highly refined wood pulp (690 D. P.) containing 0.10 P. P. M. "natural" manganese was sprayed uniformly while entering the dryer of the pulp machine with a dilute solution of manganous sulfate in such amount as to add 5 P. P. M. manganese based on bone dry pulp. This pulp was steeped in the customary manner in a caustic soda steeping liquor containing 1.5% hemicellulose and 18.5% sodium hydroxide for 30 minutes at 30° C. The alkali cellulose sheets were then pressed to a press ratio of 2.60 and shredded for 1 hour at 30° C. The alkali cellulose crumb was aged for 10 hours at 30° C. It was then xanthated for 1½ hours at 30° C. using 34% CS_2 based on cellulose in alkali cellulose. The xanthate was mixed in a dissolver for 2½ hours at 15° C. to give a viscose having the compositions of 8.5% cellulose and 5.25% sodium hydroxide. After ripening for 24 hours at 20° C., the resultant viscose had a viscosity of 35 sec. (D. P. 300), a salt index of 9.5, and gave a filtration value of 1300 g. A sample of identical pulp but without the manganese addition, processed in analogous manner, required 24 hours' aging at 30° C. to give the same viscose viscosity. Filtration values of the two viscoses and the quality factors of yarn spun from them were equivalent.

EXAMPLE II

Sheets of cellulose pulp (700 D. P.) containing manganous sulfate amounting to 10 P. P. M. manganese based on the bone dry pulp were steeped for 30 minutes at 30° C. in a caustic soda liquor containing 18.5% NaOH and 1.5% hemi, pressed to 2.6 press ratio, shredded for 60 minutes at 30° C., aged for 20 hours at 30° C., xanthated for 1½ hours at 30° C. using 34% CS_2, mixed for 2½ hours at 20° C. to give a viscose containing 10% cellulose and 5% sodium hydroxide, then allowed to ripen for 24 hours at 20° C. The viscose had a viscosity of 37 seconds, a salt index of 8.5, and gave a filtration value of 920. A similar viscose made from untreated pulp required an aging time of 50 hours at 30° C. to give a viscosity of 35 seconds. Both viscoses had the same filtration value and gave film of equivalent quality. A viscose made in similar manner from pulp treated with 1000 P. P. M. manganese but with no aging had a viscosity of 87.4, a salt index of 5.8, and gave a filtration value of 400.

EXAMPLE III

A cellulose pulp (800 D. P.) containing naturally occurring manganese compounds amounting to 2.6 P. P. M. manganese and added manganous sulfate amounting to 7.4 P. P. M. calculated as manganese was processed into viscose containing 8.5% cellulose and 5.25% sodium hydroxide. The added manganous sulfate reduced the aging requirement by two-thirds making the pulp equivalent in aging to a pulp of 600 D. P.

EXAMPLE IV

Sheets of a pulp (690 D. P.) were wetted uniformly with sufficient quantity of a dilute water solution of potassium permanganate to give 10 P. P. M. manganese in the pulp. On drying, the light pink color changed to a light brown indicating the transformation to manganese dioxide. When steeped and made into viscose this pulp showed aging characteristics similar to a pulp of 490 D. P.

EXAMPLE V

Sheets of pulp (690 D. P.) were sprayed uniformly with a dilute solution of manganese sulfate to give 50 P. P. M. in the pulp. This pulp was processed into 8.5 cellulose, 5.25 NaOH viscose in the usual manner except that the aging step was entirely omitted, sufficient viscosity reduction having occurred during steeping and shredding to give normal viscosity. The filtration value for this viscose was slightly less than for a sample containing no added manganese aged in the normal manner.

EXAMPLE VI

A web of pulp (D. P. 800) containing 0.2 P. P. M. natural manganese was uniformly sprayed while on the pulp machine with a dilute solution of manganese sulfate to give: (*a*) 5 P. P. M. manganese in the pulp making it equivalent in aging requirement to a pulp of (690 D. P.), (*b*) 10 P. P. M. manganese in the pulp making it equivalent in aging requirement to a pulp of (590 D. P.).

In similar manner a web of pulp (700 D. P.) was sprayed to give: (*a*) 5 P. P. M. manganese making it equivalent in aging requirement to a pulp of (600 D. P.), (*b*) 10 P. P. M. manganese making it equivalent in aging requirement to a pulp of (500 D. P.).

Pulps of 500 D. P. prepared from pulp of 700 D. P. by: (*a*) extra bleaching and (*b*) extra hydrolysis were inferior in quality to the 700 D. P. manganese treated pulp both initially and after viscose processing operations in which all three were reduced to a D. P. of about 400. See Table II.

EXAMPLE VII

Sheets of pulp (D. P. 1150) were sprayed with a solution of manganous acetate to give an addition of 5 P. P. M. manganese in the pulp. The aging requirement was cut in half, making it equivalent to a pulp of 800 D. P.

EXAMPLE VIII

A stock solution was made by mixing one part of a 1 gram/liter solution of manganous sulfate with 10 parts of a 10 gram/liter solution of sodium oleate. This solution containing manganese oleate together with an excess of sodium oleate was diluted and used to impregnate sheets of pulp (700 D. P.) to give 10 P. P. M. manganese and 1000 P. P. M. oleate in the pulp. The pulp then had the aging requirements corresponding to a pulp of 500 D. P.

Various compounds of manganese may be used. For reasons of economy and convenience in application the water soluble inorganic manganese compounds such as manganous sulfate, nitrate, phosphate or carbonate are very desirable. Organic compounds such as manganese acetate and compounds of low solubility such as manganese dioxide or hydroxide are also effective. Manganese may be conveniently added as the permanganate which decomposes shortly after addition to give the brown dioxide.

In certain cases a very desirable way to add manganese is to treat the cellulose, especially refined wood pulp, with a surface active manganese compound, as, for example, manganese oleate. The treatment of pulps with a wide variety of surface active compounds to improve viscose processing and spinning performance is well

known. A number of these compounds customarily used as the sodium salt may well be used as the manganese salt, thereby effecting the addition to the pulp of both manganese and surface active agent in a single operation. Although the amount of manganese required is usually much less than the amount of surface active agent customarily used, the correct amount can be obtained by correctly proportioning the manganese compound to the sodium compound in the solution, emulsion or dispersion used for treating pulp.

The manganese additions may be applied to the cellulose by any suitable method. In the treatment of wood pulp, for example, it may be applied by putting soluble manganese compounds in the wash water to be adsorbed by the pulp fibers, by dipping the pulp sheet in a dilute solution of the manganese salt, or by spraying solutions, emulsions or dispersions of the manganese compound on the pulp sheet. I prefer to spray a dilute solution of manganous sulfate onto the formed pulp sheet as it passes into the dryer on the pulp machine. It is extremely important that the amount of manganese be maintained uniform from sheet to sheet, bale to bale, and lot to lot. This is easily accomplished by means of an appropriately designed spraying system and readily checked by analysis of narrow strip samples for manganese content.

Experiments have shown that spraying is a satisfactory method for applying a uniform treat of manganese and that spraying of only one side of the sheet is sufficient. Apparently equalization of manganese among the individual fibers in a sheet occurs during steeping and shredding.

TABLE I

Effect of added manganese on viscose viscosity, index and filtration

P. P. M. Mn Added to Pulp	Aging Time and Temp., Hrs., °C.	Viscose Composition Cell-NaOH	Viscose Viscosity, Sec.	Filtration Value	Salt Index at 24 hrs.	Quality Factor of Rayon [1] (Bleached)	P. P. M. Mn in Rayon
PULP—RAYOCORD—D. P. 1150							
0	48 at 25	7.5–6.5	49.8	2490	10.0	61.2	<0.01
10	24 at 25	7.5–6.5	42.0	2535	8.5	60.4	<0.01
20	12 at 25	7.5–6.5	33.4	2080	8.2	58.5	
50	6 at 25	7.5–6.5	84.0	1240	7.0	62.4	
100	None	7.5–6.5	83.1	1000	6.0	59.2	
200	None	7.5–6.5	85.0	985	5.5	61.6	
1,000	None	7.5–6.5	92.4	525	5.3	51.4	0.10
PULP—RAYAMO—D. P. 690							
0	24 at 30	8.5–5.25	34.5	1340	9.5	40.2	<0.01
5	15 at 30	8.5–5.25	34.5	1230	9.3	41.5	<0.01
10	10 at 30	8.5–5.25	35.5	1300	9.0	40.8	<0.01
20	None	8.5–5.25	72.0	1160	8.5	42.4	
50	None	8.5–5.25	42.0	915	8.0	42.0	
1,000	None	8.5–5.25	45.3	490	6.0	38.2	
0	26 at 30	8.5–4.0	39.6	1090	8.8	38.0	
5	22 at 30	8.5–4.0	44.4	1030	8.2	37.5	
10	21 at 30	8.5–4.0	28.8	1020	8.2	37.8	
1,000	None	8.5–4.0	33.4	440	5.2		
0	50 at 30	10–5	45.0	935	8.5	37.0 43.1 [2]	
5	22 at 30	10–5	97.5	1005	8.0	37.5	
10	21 at 30	10–5	66.4	920	8.2	36.2	
1,000	None	10–5	87.4	400	5.8		

[1] Spun in regular pot machine bath 11-19-1-4—47° C.—4.2 index.
[2] Spun in 11-19-2-4 bath—52° C.—4.8 index.

TABLE II

Comparison of bleaching, hydrolysis, aging and Mn aging for reducing viscosity

	Alpha	Beta	Gamma	KOH Sol.	Cupra Visc. 2½%	Nitrate D. P.	Cellu. Yield	Viscose Viscosity (8.5-5.25 Viscose)	Viscose Filtration Value	Rayon Quality Factor
700 D. P. PULP—NO ADDED Mn—OBTAINED IN YIELD 38.0% BASED ON WOOD										
Original	88.2	5.8	6.0	10.2	3.0	690	100			
After Steeping	93.3	6.2	0.5	5.1	2.7	640	93.8			
After Shredding	91.6	7.8	0.6	5.7	2.0	550				
After Aging 20 hrs. at 30	90.1	9.3	0.6	6.0	1.2	430	92.5			
After Xanthation (Rayon)	[1] 95.2	[1] 3.6	[1] 1.2		0.9	330		45.3	1030	40.2
700 D. P. PULP—10 P. P. M. ADDED Mn—OBTAINED IN YIELD 38.0% BASED ON WOOD										
Original	88.2	5.8	6.0	10.2	3.0	690	100			
After Steeping	93.3	6.2	0.5	4.9	2.4	620	93.7			
After Shredding	92.0	7.6	0.4	5.6	1.9	500				
After Aging 4 hrs. at 30	90.0	9.4	0.6	5.3	1.2	435	92.5			
After Xanthation (Rayon)	[1] 94.9	[1] 4.0	[1] 1.1		0.9	340		50.6	1020	40.5
500 D. P. PULP—EXTRA BLEACHED—NO ADDED Mn—OBTAINED IN YIELD 37.2% BASED ON WOOD										
Original	83.4	11.6	5.0	9.3	1.4	505	100			
After Steeping	89.2	10.6	0.2	6.5	1.3	490	92.5			
After Shredding	87.2	12.6	0.2	8.5	1.3	450				
After Aging 2 hrs. at 30° C.	86.9	12.7	0.4	8.6	1.2	430	91.1			
After Xanthation (Rayon)	[1] 93.7	[1] 5.0	[1] 1.3		0.9	330		44.4	460	36.7
500 D. P. PULP—EXTRA HYDROLYZED—NO ADDED Mn—OBTAINED IN YIELD 36.8% BASED ON WOOD										
Original	79.4	16.5	4.1	17.0	1.3	480	100			
After Steeping	86.7	13.0	0.3	9.2	1.3	490	92.0			
After Shredding	85.7	13.9	0.4	8.8	1.2	450				
After Aging 2 hrs. at 30° C.	84.1	15.4	0.5	9.1	1.2	430	90.7			
After Xanthation (Rayon)	[1] 93.1	[1] 4.9	[1] 2.0		0.9	325		42.6	400	31.1

[1] Determined by special "non-dilution alpha" method.

I claim:

1. A finished refined cellulose of low aging requirements ready for conversion into viscose of good filterability which comprises manganese added as a water soluble compound in an amount varying from 1 to 100 parts per million based on the bone dry weight of the cellulose, said added manganese resulting in the refined cellulose having a uniform total quantity of manganese.

2. A finished refined wood pulp of low aging requirements ready for conversion into viscose of good filterability which comprises manganese added as a water soluble compound in an amount varying from 4 to 20 parts per million by weight based on the bone dry weight of the wood pulp, said added manganese resulting in the refined wood pulp having a uniform total quantity of manganese.

3. A finished refined wood pulp ready for conversion into viscose which comprises manganese added as a water soluble compound in an amount varying from 1 to 100 parts per million based on the bone dry weight of the wood pulp, said added manganese resulting in the wood pulp having a uniform total quantity of manganese.

4. In the production of viscose having good filterability, the improvement which comprises forming the viscose from cellulose having low aging requirements and containing from 1 to 100 parts per million of manganese added as a water soluble compound based on the bone dry weight of the cellulose.

5. In the production of viscose having good filterability, the improvement which comprises forming the viscose from refined wood pulp having low aging requirements and containing from 4 to 20 parts per million of manganese added as a water soluble compound based on the bone dry weight of the wood pulp.

6. The method of producing an improved refined cellulose of low aging requirements especially advantageous for conversion into viscose which comprises adding to the cellulose a water soluble compound of manganese in an amount varying from 1 to 100 P. P. M. of manganese and retaining in the cellulose the added manganese to impart important improvements in conversion of the cellulose to viscose, characterized by good filterability.

7. In the method of claim 6, using a refined wood pulp as the cellulose.

REID LOGAN MITCHELL.

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