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PRODUCTION OF CELLULOSIC PRODUCTS

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This invention relates to the production of cellulosic products, and has for its general object the provision of certain improvements in carrying out one or more of the processing steps in the production of such products. The invention is of special advantage in the preparation and processing of viscose derived from chemically prepared wood pulp, and in this connection aims to improve the steps of shredding, filtering and spinning viscose. The invention further contemplates, as a new article of manufacture, a chemically prepared wood pulp product having polypropylene oxide incorporated therein.

Chemically prepared wood pulps are extensively used in the industrial arts for the production of such cellulosic products as rayon and other synthetic fibers, nitrocellulose, cellulose acetate, cellulose ethers, Cellophane and similar cellulosic films or sheets etc. The wood pulp is commonly prepared and marketed in sheet form, and comminution or shredding is customarily one of the initial steps in its subsequent processing. Also even when the pulp is used in bulk form, either wet or dry, shredding or comminution will frequently be a step involved in the subsequent processing. Since such subsequent processing usually involves the conversion of the cellulose of the wood pulp to some cellulose derivative and the solution of the derivative in a suitable solvent, the purpose of shredding is to break down the sheet into a fluffy mass or crumb in which the individual fibers will be suitably exposed to the action of the derivative-forming reagent or reagents. Thus, for example, in the production of viscose the wood pulp sheet is customarily steeped in a caustic soda solution to form alkali cellulose, and the alkali cellulose, after pressing and while still in sheet form, is shredded or comminuted to properly prepare the cellulose fibers for the xanthating reaction with carbon bisulfide. The resulting sodium cellulose xanthate is dissolved in dilute caustic soda to form the solution commonly known as viscose, which is opacified if desired, and spun into filaments.

Normal dissolving wood pulps in present use consist mainly of cellulose, but contain appreciable amounts of non-cellulosic impurities, such as hemi-celluloses, fats, resins, waxes etc. One of the main objects in the manufacture of a highly refined dissolving pulp is to remove as much as possible of the non-cellulosic impurities, so that a whiter, purer pulp results, which is capable, in the manufacture of rayon, of producing a higher grade yarn.

We find, however, that not all of the non-cellulosic impurities which can be removed are undesirable, and, in fact, certain of such impurities, normally present in small amounts, are highly beneficial in aiding the processing of the pulp into viscose, especially as regards the step of shredding the alkali cellulose. These beneficial impurities which aid the shredding operation are probably of the nature of fiber lubricants which permit the steeped and pressed pulp to be thoroughly shredded into a fluffy condition more readily and without mechanical damage to the alkali cellulose fibers which would cause them to react incompletely with carbon bisulphide. In a pulp which has not been highly refined, these beneficial impurities constitute a portion of the materials removable by organic solvents, as, for example, ether, benzene, alcohol etc. These beneficial impurities, often loosely termed "resins," are mainly of the nature of waxes and fats, together with some true resins, the latter often being present in a relatively small amount.

In theory, the problem of making a good pulp could be solved by removing all the undesirable impurities while retaining those impurities which facilitate the shredding operation by lubricating the fibers or otherwise. In practice, such a clean-cut separation is difficult to accomplish directly. We have discovered that better results are obtainable by removing most or all of the impurities including those which serve beneficially as lubricants to the alkali cellulose fibers during shredding, and then adding to the pulp or to the alkali cellulose prior to the completion of shredding a sufficient amount of an agent capable of acting like, and actually being more effective than, the natural beneficial impurities.

White, highly purified or refined wood pulps are very advantageous for the production of high grade rayon yarns of superior strength and color, and, for this reason, are highly esteemed by the trade. Such highly refined pulps are in general characterized by having an ether extract of about 0.15% or less where such percentage refers to the amount of natural ether extractable material left in the pulp after the purification processes. While our invention is particularly applicable to such highly refined pulps containing not more than about 0.15% of ether extractable material, it may be applied with certain advantages to the processing of normal dissolving pulps containing substantially more than 0.15% of ether extractable material, although such pulps do not generally yield the highest grade yarns and their processing into shredded alkali cellulose is not accompanied by any particular difficulty.

We have discovered a class of agents, namely polypropylene oxides, which lubricate or protect the alkali cellulose fibers during shredding, and which are chemically entirely different from the beneficial impurities naturally present in the pulp. In general, they are much more effective in promoting shredding than the beneficial impurities naturally present in the pulp. Moreover, these agents exercise a beneficial influence upon certain subsequent steps in the preparation

and processing of the viscose into rayon which the natural beneficial impurities do not exercise. Based on these discoveries, our invention involves improving one or more of the processing steps in the production of cellulosic products from chemically prepared wood pulp by carrying out the processing step in the presence of polypropylene oxide. When applied to the preparation and processing of viscose derived from chemically prepared wood pulp, the invention particularly involves carrying out the shredding of the alkali cellulose, or at least the final stage of shredding, and the spinning of the viscose in the presence of a polypropylene oxide. Where the invention is practiced solely to improve the spinning of the viscose, it is immaterial from what cellulosic raw material the viscose is derived.

Polypropylene oxides are known to have been prepared by polymerizing propylene oxide with water in the presence of a suitable catalyst, such as sodium hydroxide, or by carrying out the polymerization under anhydrous conditions in the presence of a catalyst such as stannic chloride. Products prepared in the presence of sodium hydroxide and water, which are the most preferred compounds for use in our invention, are believed to have the empirical formula $(CH_3C_2H_3O)_n.H_2O$. In the case of the use of other catalysts the nature of the terminal groups is not always certain but in a long chain a small end group has an inconsequential effect. The polymerized products are viscous liquids to semi-solids, the liquids or melted products being of varying viscosity depending upon the degree of polymerization. The solubility in water also varies with the degree of polymerization, the products ranging in solubility characteristics from highly soluble through slightly soluble to substantially insoluble as the degree of polymerization increases. As normally prepared, the polymerized products are not homogeneous compounds, but are mixtures of various chain lengths or degrees of polymerization. Each product, however, even though a mixture will obviously have a mean or predominating chain length so that the product as a whole may be considered as having a certain degree of polymerization. The polyoxypropylene glycols (sometimes termed "polypropylene glycols") which can be prepared by condensation reactions so as to be homogeneous in regard to chain length are believed to be structurally identical with polypropylene oxides prepared in the presence of water and sodium hydroxide and are equally suitable for the practice of our invention, and are intended to be included within the generic designation of polypropylene oxides. The generic designation, however, does not include volatile non-viscous cyclic derivatives such as dimethyl dioxane which are not generally considered to be polypropylene oxides.

We have found that all polypropylene oxides including even the simplest products, such as dipropylene glycol, are operative as regards their use in our invention. In practice, however, we find that there are advantages in using polypropylene oxides having degrees of polymerization falling within certain well-defined limits, as hereinafter described in detail. With polypropylene oxides, as with most other polymers, increase in the degree of polymerization is accompanied by a rise in the viscosity of the products. In characterizing the degrees of polymerization, which in the case of non-homogeneous polymers are actually the mean or effective degrees of polymerization, we prefer to use the specific viscosity as measured in benzene solution, since such determinations may be readily and accurately carried out. The specific viscosity of a solution of a given concentration is calculated according to the well-known equation $\eta_{sp}=\eta_r-1$, where η_r is the relative viscosity of the solution referred to the pure solvent. In particular, in characterizing polypropylene oxides we prefer to use the specific viscosity as measured in a 4.0% benzene solution by weight at 18° C., the value so obtained being hereinafter termed the "specific viscosity."

In regard to the aspect of our invention which involves the improving of the shredding operation so that a viscose solution with improved filtration characteristics results, all polypropylene oxides, including even the simplest products, are quite effective. Those products which have a specific viscosity of at least 0.065 are, however, the most effective as regards this aspect of our invention. Since polypropylene oxides with a specific viscosity of 0.065 have a comparatively low degree of polymerization, the products which are most effective in improving viscose filtration, i. e., those having specific viscosities of at least 0.065, will cover a wide range in regard to degree of polymerization. From a practical standpoint, however, having particular consideration for the solubility properties in caustic soda solutions and in water as well as for the effect of the products on spinning, we prefer for purposes of improving filtration to use a more restricted range of specific viscosity as explained later in detail.

As regards the aspect of our invention which contemplates the minimizing of incrustations in the orifices of spinnerets, the effective limits of specific viscosities range from about 0.069 to 0.584. Above and below these limits only very small reductions in the formation of incrustations are obtained. For the most effective results in the minimization of incrustations, however, as well as for other practical reasons discussed later, we prefer to use polpropylene oxides falling within a considerably more restricted range of specific viscosities, namely about 0.083 to 0.138.

Polypropylene oxides for use in practising the invention may be prepared from propylene oxide by any of the methods known to the art, such as treatment with stannic chloride, or treatment at an elevated temperature for a suitable time with caustic soda solution. The methods of preparation which we have found convenient and prefer to use are given for purposes of illustration though it is to be distinctly understood that the invention is not confined to the use of polypropylene oxides prepared by any particular method. All polypropylene oxides are operative in our invention and even in regard to our prefered range of specific viscosities it is obvious that a polypropylene oxide of a given specific viscosity will be equally effective irrespective of the method of its preparation.

We prefer to heat propylene oxide with a small proportion of caustic soda solution of about 48% strength with agitation in a sealed vessel or autoclave at a temperature of about 95° to 150° C. until the pressure drops to substantially atmospheric pressure or drops markedly from the peak pressure which will be in the neighborhood of the theoretical vapor pressure of the propylene oxide to a substantially lower and approximately constant value. In preparing polypropylene

oxides of relatively low molecular weight, a reaction temperature of about 100° C. is very suitable. In carrying out the polymerizations at such a temperature, the pressure will finally drop to substantially atmospheric pressure. In preparing products other than those with very low degrees of polymerization, in order to have the reaction go to completion in a reasonable time it will be usually more practical to operate at higher temperatures than 100° C. In operating at such high temperatures, e. g., 135°–150° C., the pressure may not finally drop in all cases completely to atmospheric pressure, due to the formation of small amounts of volatile decomposition products. The completion of the reaction in such cases, however, can be readily recognized by a marked drop in pressure to an approximately constant low value. Furthermore, the formation of small amounts of volatile propylene oxide decomposition products does not essentially alter the effectiveness of the products for the purposes of the invention.

In polymerizing propylene oxide with 48% caustic soda solution at a given temperature, the smaller the proportion of caustic soda solution the higher will be the degree of polymerization, and the higher will be the specific viscosity. Also, using a constant proportion of caustic soda solution within the temperature range of 95° to 150° C., the higher the temperature, the higher will be the degree of polymerization and the higher the specific viscosity. Polymerization products obtained by the use of caustic soda solution will contain the original amount of alkali which will not be objectionable if the agent is to be added directly to the viscose. If, however, the material is to be added to the pulp prior to use, it is advisable to eliminate the alkalinity. This may readily be accomplished by adding concentrated hydrochloric acid or 35% sulphuric acid to the molten polypropylene oxide removed from the autoclave until neutralization is obtained.

While purification is not necessary for the purposes of the invention itself, the polymerized products should undergo further purification in addition to neutralization, if it is desired to characterize them accurately by their specific viscosities. A suitable method of purification may include dissolving the neutralized material in a suitable solvent such as benzene, removal of water by addition of a suitable drying agent such as sodium sulphate, removal of inorganic salts from the water-free solution by filtration and removal of the solvent by vacuum distillation. In addition to the foregoing treatment, the product while in benzene solution may be decolorized by the addition of decolorizing charcoal or activated carbon.

Stannic chloride is known to be very effective in promoting the polymerization of propylene oxide. We believe, however, that polymerization by use of stannic chloride in general is inferior to the method outlined above, using caustic soda, for a number of reasons; in particular with stannic chloride there is a certain danger of explosion. The initial reaction with stannic chloride is very violent and hard to control, and the tendency is to yield a more heterogeneous product than that obtained by use of caustic soda as catalyst. The use of stannic chloride does, however, permit the more ready preparation of products having a very high degree of polymerization than does the use of caustic soda. Where stannic chloride is to be used, we prefer to add the required amount of stannic chloride to the propylene oxide with constant stirring and cooling and then after the initial energy of the reaction is spent to heat the mixture in an autoclave with agitation about 100° C. until the reaction is completed. In general the lower the proportion of stannic chloride the higher will be the molecular weight. Before using products prepared thus for the purposes of our invention they should preferably be de-tinned. This may be readily accomplished by boiling the materials with water, whereupon the tin soon separates out as a white precipitate, presumably stannic hydroxide. With high molecular weight products which are relatively water insoluble, the de-tinned material floats and is easily separated off and filtered. This is a simple, practical procedure. Where, however, the products are to be accurately characterized by their specific viscosities, we prefer to extract the de-tinned product (whether relatively insoluble in water or not), from the mixture with benzene, and then to treat the benzene solution in the same manner as with similar solutions obtained when purifying products obtained by the use of caustic soda as catalyst.

The table below gives the specific viscosities and solubility properties of the products obtained using varying amounts of 48% caustic soda or of stannic chloride as catalyst together with 50 grams of propylene oxide under various reaction conditions. The products, in addition to being neutralized or de-tinned as described, all went through the additional outlined purification procedures involving solution in benzene in order to eliminate inorganic materials and water making possible accurate characterization by viscosity measurements.

TABLE

Properties of polypropylene oxides prepared under various conditions

Cc. catalyst used per 50 gm. propylene oxide	Reaction conditions		Properties of product	
	Temperature, ° C.	Time, hours	Specific viscosity [1]	Solubility in water [2]
A. USING STANNIC CHLORIDE AS CATALYST				
0.5	[3] 100	112	0.584	Insoluble.
2.0	[3] 100	6	0.129	Partly insoluble.
B. USING 48% NaOH AS CATALYST				
0.25	120–150	18	0.137	Soluble with turbidity plus small amount of suspended globules.
0.125	135	18	0.138	Same as above.
0.5	135	11	0.124	Do.
2.0	135	6	0.083	Soluble with turbidity.
0.5	123	14	0.113	Do.
0.5	116	22	0.083	Do.
0.25	100	74	0.106	Clearly soluble.
0.91	100	9	0.079	Do.
4.0	100	3.75	0.069	Do.
8.0	100	3	0.065	Do.

[1] The specific viscosity was determined for 4% solutions by weight in benzene at 18° C.

[2] For the solubility tests, six drops of polypropylene oxide were added to 15 cc. of water, the mixture was vigorously shaken and then allowed to stand at room temperature.

[3] The reaction mixtures were not heated until the initial energy of reaction was spent.

While highly refined wood pulps are advantageous for the production of high grade rayon yarns of superior strength and color, the reaction of the shredded alkali cellulose from such pulps with carbon bisulfide is frequently incomplete. This impairment in the xanthating activity of

the shredded alkali cellulose is due to some damage to the fibers during the shredding operation or to incomplete comminution or to formation of compressed fiber bundles. In the case of the conventional shredder having revolving blades coacting with a stationary saddle bar, the tendency for such damage is especially great if the clearance between the revolving blades and the saddle bar is a little less than the correct value. In an extreme case, with a very highly refined pulp, shredding, even under optimum conditions, may produce a shredded pulp which xanthates less completely than if the alkali cellulose were not shredded at all. In other cases, it is possible to obtain reasonably satisfactory shredding of the alkali cellulose from highly refined pulps by adjusting the shredder clearance and by experimenting to find the optimum shredding time for the particular pulp and particular shredder. In this manner it is possible in some cases to obtain almost as complete a degree of xanthation of the shredded alkali cellulose from a highly refined pulp as would be obtained with the shredded alkali cellulose from a less pure pulp. But the necessity of constant supervision and adjustment to assure optimum shredding conditions makes the shredding of highly refined pulps too sensitive for satisfactory commercial practice. This sensitivity to damage during shredding of the alkali cellulose from highly refined pulps is overcome, in our invention, by carrying out the shredding operation in the presence of polypropylene oxide which may be added to the pulp prior to shredding or to the alkali cellulose during shredding and prior to the completion of shredding. While the invention thus improves the shredding operation, the most noteworthy evidence of this improvement is in the subsequent filtration of the viscose. The improvement in shredding produces a shredded alkali cellulose which reacts substantially completely with carbon bisulfide, and the resulting viscose is comparatively free of unreacted fibers and filtration proceeds more rapidly and economically.

In the spinning of viscose into acid spin baths containing certain metallic salts and especially a zinc salt, incrustations or craters tend to form within the orifices of the spinneret, either partially or completely blocking the orifices. The partial blocking of the orifices causes objectionable irregularities in the thickness of the filaments and frequently causes breaking of the filaments which necessitates interruption of the spinning operation to change spinnerets. The formation of such incrustations or craters is suppressed or minimized in the present invention by carrying out the spinning operation in the presence of polypropylene oxide. The polypropylene oxide may be added to the viscose or to the constituents entering into the production of the viscose, or may be added to the acid spin bath.

While this phase of our invention relates primarily to improving spinning conditions in the viscose process where viscose is normally extruded through spinnerets or other orifices into acid setting baths it is to be understood that the invention is not limited to the viscose process, but is applicable to any process where cellulosic solutions are extruded through spinnerets or other orifices into aqueous setting baths, where incrustations tend to form within the extrusion orifices. In such cases, the invention is only subject to the limitations that the material be added in such a way as to be present in either the spinning solution or spin bath at the time of spinning.

When polypropylene oxide has been employed to improve shredding, in accordance with the invention, the polypropylene oxide will be present in the resulting viscose. Although, as hereinafter more particularly explained, the amount of polypropylene oxide required for securing the contemplated improvement in suppressing or minimizing crater formation during spinning is slightly greater than the amount required for securing the contemplated improvement in shredding and filtration, there is no objection to carrying out the shredding step in the presence of such amount of the polypropylene oxide as is required in the spinning of the viscose. Indeed, the full advantages of our invention are best realized when the polypropylene oxide is added to the pulp, or to the alkali cellulose prior to the completion of shredding and in amount adequate for securing the contemplated improvement in spinning of the viscose.

The most practical and economical manner of securing the desired presence of a polypropylene oxide during the shredding of the alkali cellulose and during spinning of the viscose is to incorporate the polypropylene oxide in the wood pulp. This may be advantageously effected by adding the polypropylene oxide to the pulp on the sheet-forming machine subsequent to sheet formation but prior to complete drying, by spraying the pulp sheet with an aqueous solution or emulsion of the polypropylene oxide or by means of a rotating roll partly immersed in such a solution or emulsion. If desired, the polypropylene oxide may be incorporated in the pulp prior to sheet formation, as, for example, by adding the agent to a suspension of pulp in water in a stock chest. In the latter case, the white water should be re-circulated in order to prevent considerable loss of the agent when eliminating water in sheet formation. In any case, there is produced a chemically prepared wood pulp product having polypropylene oxide incorporated therein. The production of this product, as a new article of manufacture, is one of the improved aspects of the invention. When the agent is so incorporated in the wood pulp, by the manufacturer thereof, the pulp comes to the rayon manufacturer in a form calculated to secure the full advantages of the invention in the preparation and processing of the viscose into high grade rayon yarns.

We have found that with polypropylene oxides prepared by the use of caustic soda solutions, products having specific viscosities up to about 0.083 to 0.106 (the exact point depending somewhat on the temperature of preparation) are either clearly soluble in water, or soluble with only slight turbidity. Products having specific viscosities intermediate between these values and a value of about 0.124 are generally soluble in water with appreciable turbidity. Polypropylene oxides with specific viscosities of about 0.124 to 0.138 are largely readily soluble in water with turbidity but the freshly prepared solutions usually contain a very small proportion of suspended small insoluble globules visible to the naked eye and which will eventually settle out. Such solutions are, however, very effective and the presence of a small proportion of water-insoluble liquid matter appears to be in no wise harmful as regards their operativeness in the viscose process. A small amount of water-insoluble material may, however, be undesirable practically as regards the mechanics involved in treating a pulp sheet with such a solution, especially if the treat is applied by means of fine sprays rather than by means

of a roll dipping in a trough. In such a case the insoluble matter can be readily removed by filtering the solution or can be readily dispersed in the solution by adding a very small proportion of a surface active emulsifying agent. In general, polypropylene oxides having viscosities appreciably greater than 0.138 are relatively insoluble in water, the degree of water insolubility increasing with the specific viscosity. Where the pulp is to be treated incident to its manufacture, it would be possible to apply such relatively water-insoluble polypropylene oxides from a solution in a suitable organic solvent such as commercial denatured alcohol or from a mixture of alcohol and water. Practically, however, it will be considerably more economical to emulsify the materials in water in the presence of a small amount of a surface active emulsifying agent.

Where the shredding operation is to be improved by adding the agents during shredding, products which are water soluble may be either sprayed into the shredder as a strong aqueous solution or simply added without any dilution. With those products which are insoluble in water, it will be usually most convenient to add them in the undiluted state. When adding the undiluted liquid products, it is only necessary to obtain a rough distribution over the alkali cellulose since the polypropylene oxides possess the property of spreading rapidly over the alkali cellulose fibers during the shredding operation. With very high molecular weight products which are normally semi-solid at ordinary room temperatures, it will be found advisable to melt them by warming prior to addition. When it is desired only to improve the spinning operation and the agents are to be added directly to the viscose, they may be suitably added either as aqueous solutions or in the undiluted form. Products which are relatively water insoluble are most conveniently added to the viscose in the undiluted state and through mixing readily become dispersed.

Polypropylene oxides prepared by use of stannic chloride, possibly due to the powerful nature of the catalyst, normally are more heterogeneous in regard to the degrees of polymerization of the components than are products prepared by the use of caustic soda, according to the methods outlined. For example, the polypropylene oxides shown in the table, which was prepared by the use of stannic chloride and had a specific viscosity of 0.129, was relatively heterogeneous in that a portion was substantially soluble in water while a considerable portion was substantially insoluble in water. Nevertheless, the product was generally very effective both in regard to improving filtration and in regard to minimizing incrustations during spinning. In view of the partial water insolubility, this particular product was applied to the pulp either as a solution in a mixture of alcohol and water, or as an emulsion in water. In applying the product to the alkali cellulose during shredding, it was added in the undiluted state.

The solubility of the polypropylene oxides in the sodium hydroxide concentrations present in steeping, e. g., about 18%, decreases as the degree of polymerization increases, and polypropylene oxides having a specific viscosity of at least 0.083 measured as hereinbefore described, are relatively insoluble in 18% sodium hydroxide. However, the presence during steeping of a polypropylene oxide having a specific viscosity lower than 0.083 results in the solution of the agent in the sodium hydroxide steeping liquor in amounts varying with the agent's solubility. Since the steeping liquor is repeatedly used, it soon becomes saturated with the agent and the loss of the agent in pressing the steeping sheets becomes practically unimportant. However, more uniform and dependable results are obtained by employing agents substantially insoluble in sodium hydroxide concentrations of around 18%, i. e., those having specific viscosities of at least 0.083. Moreover, those polypropylene oxides having specific viscosities of from about 0.083 to 0.138 are the most effective in bringing about the contemplated improvements in the spinning operation. Again, so long as the products are prepared by methods which do not tend to give very heterogeneous products, those products which have specific viscosities not exceeding about 0.138 will be substantially water soluble and hence the mechanics involved in their application will be economical and convenient. Again, in regard to improving filtration, the range of from 0.083 to 0.138 is also part of the broad range giving maximum filtration improvement. Accordingly, it is our preferred practice, especially when the agent is to be added to the pulp prior to steeping, to employ in the practice of the invention polypropylene oxide having a specific viscosity of at least 0.083 and preferably not appreciably exceeding 0.138.

The amount of polypropylene oxide used in the practice of the invention is relatively small, ranging from 0.01 to 0.25%, and preferably from 0.02 to 0.15% by weight on the bone dry weight of the pulp. So far as the objectives of the invention are concerned, there is little if any improvement by increasing the amount of the polypropylene oxide above 0.25%, and such higher amounts give rise to certain disadvantages. These disadvantages include the causing of excessive softness in the sheet, resulting in mechanical difficulties in steeping, excessive ball formation in xanthation, difficulties in the dissolving operation due both to the excessive ball formation in the xanthating step and due to excessive foaming in the viscose solution. Also there will be considerable difficulty in obtaining a completely deaerated viscose which is absolutely necessary for satisfactory spinning. Higher concentrations of the polypropylene oxide also unduly lower the surface tension of the viscose, thus changing the coagulating conditions so that the viscose cannot be satisfactorily spun by standard methods, causing the filaments to break and the thread to stick to the godet wheels or thread guides.

The amount of polypropylene oxide required for securing the contemplated improvement in shredding and filtration is generally slightly less than the amount required for securing the contemplated improvement in suppressing or minimizing crater formation during spinning. Thus, the contemplated improvement in shredding and filtration will generally be brought about by from 0.02 to 0.05% of the polypropylene oxide, and rarely would more than 0.1% be required. For suppressing or minimizing crater formation the polypropylene oxide should be present in either the viscose or the spin bath in amount of 0.1% or even higher. These percentage figures are based on the bone-dry weight of the pulp used. When the polypropylene oxide is incorporated in the spin bath, the amount present in the spin bath may advantageously be 0.001 to 0.1% by weight on the weight of the bath.

While it is our preferred practice to incorporate the polypropylene oxide in the wood pulp

product, which preferably is a highly refined pulp containing not more than about 0.15% of ether extractable material and is commonly marketed in sheet form, the presence of the agent during the processing steps of shredding, filtering and spinning may be secured in any other appropriate manner. Moreover, the agent need not be incorporated in every sheet of pulp, but may be incorporated in only alternate sheets, or may be otherwise added to only a portion of the pulp in whatever form it is marketed. Alternatively, the agent may be sprayed upon or otherwise suitably added to all or a portion of the alkali cellulose prior to shredding or prior to the completion of shredding. Finally, in those cases where the invention is not practiced in the shredding and filtering steps, the polypropylene oxide may be incorporated in the viscose or the spin bath, and in such cases the suppressing and minimizing of crater formation will be attained where the viscose is made of cellulosic raw material other than wood pulp. However, we believe it will generally be found more advantageous to incorporate the polypropylene oxide in the initial wood pulp product both as a matter of convenience and economy in preparing and processing the viscose, and because a very uniform distribution of the agent throughout the viscose is easily attained.

When the invention is practiced for effecting the hereinbefore mentioned improvements in shredding and filtering, certain further economies are effected in the subsequent steps of xanthating, dissolving and filtering. In viscose solutions there is usually a certain amount of undissolved fibers and gel-like material due to the incomplete reaction of the cellulose with the carbon bisulfide during xanthation. Prior to spinning, the viscose solutions are filtered several times to remove these gels and undissolved fibers. In the event that the viscose solutions contain excessive amounts of undissolved and partially dissolved fibers, filtration is an expensive operation. In such cases the filters become rapidly clogged and the filter media must be changed frequently in order that the viscose will pass through in a reasonable time. Frequent changing of the filter media is expensive, not only as regards consumption of filter cloth but also in view of the very considerable amount of labor involved and also since a certain amount of viscose is lost every time the filter is opened up. Furthermore, when the viscose solutions contain very large proportions of gel-like material, filtration is usually not altogether satisfactory in that some of the smaller gel-like particles tend to pass through the pores of the cloth with adverse effect upon the spinning operation. It has heretofore been the practice in the viscose industry, when processing pulps which tend to yield viscose solutions high in undissolved material and having poor filtration properties, to minimize such difficulties by carrying out the xanthation with amounts of carbon bisulfide considerably in excess of that normally required. Use of excess carbon bisulfide is expensive and in addition is technically undesirable in that it may adversely affect certain properties such as the ripening of the viscose and yarn characteristics. We have found that when processing highly purified pulps which would normally tend to give poorly filtering viscose solutions, the addition of minute amounts of polypropylene oxide so improves the shredding operation that the alkali cellulose subsequently reacts much more completely with carbon bisulfide and yields a viscose solution very free from undissolved and partially dissolved cellulose particles and having good filtration properties. This result can be accomplished not only without the use of excess carbon bisulfide, but in many cases satisfactory viscose solutions can be obtained using amounts of carbon bisulfide very substantially less than the amounts normally required.

We claim:

1. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp which comprises adding prior to the completion of shredding the alkali cellulose a polypropylene oxide.

2. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp which comprises adding prior to the completion of shredding the alkali cellulose a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C.

3. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp which comprises adding prior to the completion of shredding the alkali cellulose a polypropylene oxide having a specific viscosity around 0.083–0.138 measured in a 4% benzene solution by weight at 18° C.

4. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp which comprises adding prior to the completion of shredding the alkali cellulose from 0.01 to 0.25% of polypropylene oxide based on the bone dry weight of the pulp.

5. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp which comprises adding prior to the completion of shredding the alkali cellulose from 0.02 to 0.15% of a polypropylene oxide based on the bone dry weight of the pulp, the polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C.

6. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp containing not more than about 0.15% ether extractable material which comprises adding prior to the completion of shredding the alkali cellulose a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C., the amount of the polypropylene oxide present being from 0.01 to 0.25% by weight on the bone dry weight of the pulp.

7. The method of improving a processing step in the production of regenerated cellulosic products by the viscose process from chemically prepared wood pulp containing not more than about 0.15% ether extractable material which comprises adding prior to the completion of shredding the alkali cellulose a polypropylene oxide having a specific viscosity around 0.083–0.138 measured in a 4% benzene solution by weight at 18° C., the amount of the polypropylene oxide present being from 0.02 to 0.15% by weight on the bone dry weight of the pulp.

8. The method of improving chemically prepared wood pulp which comprises incorporating in the wood pulp a polypropylene oxide.

9. The method of improving chemically pre-

pared wood pulp which comprises incorporating in the wood pulp a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C.

10. The method of improving chemically prepared wood pulp which comprises incorporating in the wood pulp a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C., the amount of the polypropylene oxide present during each of said steps being from 0.01 to 0.25% by weight on the bone dry weight of the pulp used for preparing the viscose.

11. As a new article of manufacture, a wood pulp having a relatively small amount of a polypropylene oxide incorporated therein.

12. As a new article of manufacture, a wood pulp having incorporated therein from 0.01 to 0.25% of a polypropylene oxide based on the bone dry weight of the pulp.

13. As a new article of manufacture, a chemically prepared wood pulp containing not more than about 0.15% ether extractable material and having incorporated therein from 0.01 to 0.25% of a polypropylene oxide based on the bone dry weight of the pulp.

14. As a new article of manufacture, a wood pulp having incorporated therein a relatively small amount of a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C.

15. As a new article of manufacture, a wood pulp having incorporated therein a relatively small amount of a polypropylene oxide having a specific viscosity around 0.083–0.138 measured in a 4% benzene solution by weight at 18° C.

16. As a new article of manufacture, a chemically prepared wood pulp containing not more than about 0.15% ether extractable material and having incorporated therein a polypropylene oxide having a specific viscosity of around 0.065–0.584 measured in a 4% benzene solution by weight at 18° C., the amount of the incorporated polypropylene oxide being not less than 0.01% by weight on the bone dry weight of the pulp.

17. As a new article of manufacture, a chemically prepared wood pulp containing not more than about 0.15% ether extractable material and having incorporated therein a polypropylene oxide having a specific viscosity around 0.083–0.138 measured in a 4% benzene solution by weight at 18° C., the amount of the incorporated polypropylene oxide being from 0.01 to 0.25% by weight on the bone dry weight of the pulp.

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