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METHOD OF IMPROVING THE PROCESSING
OF REFINED CHEMICAL PULP INTO VIS-
COSE BY ADDING CATION ACTIVE AGENTS

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Our invention relates to improving the process-
ing of refined chemical pulp into viscose by add-
ing cation active agents.

More particularly our invention relates to the
adding of cation active agents to refined chemical
pulp or to one of the viscose forming materials at
a stage prior to completion of xanthation to pro-
vide an improved viscose solution. These solu-
tions in turn are designed to be used in further
manufacturing processes. The viscose solutions
resulting from our invention or discovery may be
employed in the manufacture of cellulose prod-
ucts, as artificial yarn or rayon, staple fiber,
transparent films, or sausage casings.

While our invention relates primarily to im-
provements in the preparation of cellulose solu-
tions by the viscose process, it should be under-
stood that the principles involved are of a broad
nature and may be applied also to the prepara-
tion of cellulosic solutions of other types, such
as cuprammonium solutions of cellulose and so-
lutions of cellulose derivatives, such as cellulose
acetates, nitrates or ethers.

In all these instances the objective is to bring
the cellulose into proper solution and the provid-
ing for this constitutes the primary object of our
invention.

Specifically our invention provides a great im-
provement in most of the steps, such as shred-
ding, xanthating, dissolving, filtering, and emul-
sifying or dispersing, which steps are involved in
forming viscose solutions and preparing the
same for use for further manufacturing proc-
esses.

Accordingly, for purposes of definiteness and
clearness of description and illustration, our in-
vention will be set forth as respects the steps in-
volved in forming viscose solutions and preparing
the same for use in further manufacturing proc-
esses, but it is to be understood that the invention
is not to be limited to any such specific applica-
tion.

In general, our invention, for a summary state-
ment, may be said to relate to treating with cer-
tain cation active agents the pulp or one or more
of the viscose forming materials at any stage
prior to the completion of xanthation while such
pulp is being formed into a solution by the vis-
cose process.

The procedure in preparing viscose solutions
ordinarily involves the treatment of cellulose with
caustic soda of about 18% concentration, then
with carbon bisulphide and finally dissolving the

xanthated fibers resulting in a cellulosic solu-
tion with a caustic content of 5-8%. Since the
viscose solution is essentially a cellulose solu-
tion, therefore it is desirable to keep all additions
of foreign agents to an absolute minimum. Ob-
viously, if any agent is to be added it should be
present in very minute quantities and the ques-
tion then arises as to whether it would be effec-
tive. Our invention comprises the discovery of
agents which are very effective in greatly im-
proving the preparation of the viscose, even when
employed in very minute quantities and which
at the same time are not otherwise objectionable.

In the customary manufacture of viscose solu-
tions from refined chemical pulp for the spinning
of artificial yarn or rayon, the pulp is subjected,
in general, to the following steps, and the purpose
of these steps is mainly as indicated:

Steeping.—The first step in the viscose rayon
process is known as steeping. Its purpose is main-
ly twofold, (1) to provide the pulp fibers with a
certain amount of caustic soda necessary in the
xanthating step and (2) to dissolve out certain
impurities such as hemicelluloses. In steeping,
the pulp, commonly employed in sheet form, is
immersed in caustic soda solutions of merceriz-
ing strength, as commonly used about 18%, and
thereafter removed and subjected to pressing to
eliminate part of the adhering caustic soda, to-
gether with the greater part of the dissolved im-
purities. The product after steeping is known as
alkali cellulose. The action of the caustic soda in
this steeping process should be uniform and com-
plete, otherwise there would be parts of the fibers
improperly prepared for xanthating.

Shredding.—The second step in the viscose
process is that of shredding the alkali cellulose.
Its purpose is the comminution of the sheet struc-
ture which still remains on completion of the
steeping process. One object of this comminution
is to properly expose the individual fibers to the
action of oxygen for proper alkali cellulose age-
ing, i. e., to permit the lowering of viscosity. A
second purpose of this comminution is to expose
all portions of the fiber so that in the xanthating
step where carbon bisulphide is added, all of the
individual fibers will be completely treated.

Ageing.—The alkali cellulose after being shred-
ded is kept for a certain time at a definite tem-
perature depending on the viscosity and proper-
ties desired in the viscose at later periods of the
process. This step is known as ageing of the al-
kali cellulose and involves essentially changes in

the cellulose molecules or aggregates so that lower viscosities result.

Xanthating and dissolving.—On completion of the ageing period, the alkali cellulose is treated with carbon bisulphide to form sodium cellulose xanthate, a process called xanthation. The xanthated cellulose is properly formed, dissolves readily in dilute caustic soda to form the solution commonly known as viscose.

Ripening.—Immediately on solution of the xanthated cellulose in dilute caustic soda, certain chemical reactions take place, which gradually alter the chemical and physical properties of the viscose. These reactions are allowed to proceed to a definite extent under controlled conditions in order to impart the desired properties to the viscose necessary for satisfactory spinning. This operation is known as viscose ripening.

Filtering.—In the viscose solution there is usually a certain amount of undissolved fibers and gel-like material due to incomplete reaction of the cellulose fibers with the carbon disulphide during xanthation. In the course of the ripening period the viscose solution is filtered several times to remove these gels and undissolved fibers. This is of importance as otherwise the fine openings in the spinnerets through which the viscose is extruded during the subsequent spinning process would soon become clogged.

Emulsifying or dispersing.—If the viscose solution is spun without further treatment, a high lustre yarn results. In many cases it is desirable to manufacture a yarn with subdued lustre, and this result may be obtained by emulsifying or dispersing small amounts of mineral oil or other immiscible materials in the viscose. Naturally it is of importance that these emulsions or dispersions be characterized by uniform minuteness of particle size in order to avoid breaking or weakening of the filaments by the interruption of the constant flow of viscose through the minute orifices of the spinneret. Further, the emulsions or dispersions must be characterized by extreme stability, in that they must not deteriorate during the period required for viscose ripening.

Normal dissolving pulps in present use consist mainly of cellulose but contain appreciable amounts of non-cellulosic impurities such as hemicelluloses, fats, resins, waxes, etc. One of the main objects in the manufacture of a satisfactory 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 general of producing a higher grade yarn.

We find, however, that not all the non-cellulosic materials which can be removed are undesirable and in fact that certain of such impurities normally present in small amounts are highly beneficial in the steps involved in the preparing of the viscose solution. These beneficial impurities for the most part are surface active materials or materials which can give rise to the production of surface active materials during the steps of steeping or the other steps prior to completion of xanthation in the manufacture of rayon. In a pulp which has not been highly refined, these beneficial substances which are of the nature of fats, resins and waxes constitute a portion of the materials which are removable by organic solvents, for example ether, benzene, alcohol, etc. In general we find there is a direct relationship between filtration of the viscose and the ether extract of the pulp.

In theory, the problem of making a good pulp would be solved by removing all the undesirable, and retaining all the desirable substances. In practice, such a clean-cut separation is difficult to accomplish directly. We have discovered that better results are obtained by removing most of or all the undesirable materials without regard to the beneficial portion thereof and then to add to the pulp a sufficient amount of materials or agents having a similar action to the natural beneficial portion. In general, our invention is particularly concerned with those pulps which do not have remaining more than 0.15% of natural ether extractable material. Pulps of this degree of purification present the problems hereinabove set forth and constitute the base or starting material to which the agents of our invention are applied.

We have discovered that there are agents, some chemically similar to, and some chemically different from, that portion of the impurities naturally present providing beneficial action. In general the agents which we have discovered are much more effective than the beneficial portion of the impurities naturally present. Accordingly, the compounds or agents of our discovery can be used in very minute quantities. This is doubly advantageous, because such additions of materials are inexpensive and also because the very pure pulp treated with our agents is substantially free from non-cellulosic materials due to the minuteness of the quantity of the agents required.

The surface active portion of the beneficial impurities, naturally present as such in the refined pulps or formed during the processing, are predominately of the general class known as anion active materials. By "surface active agent" we mean, for purposes herein set forth, such "surface active agents" which are at least dispersible in viscose solutions.

We have made a very important discovery in that we find that we can obtain very substantial improvements in the preparation of viscose from a refined chemical dissolving pulp by adding prior to the completion of xanthation surface active materials of an entirely different class from those surface active materials naturally present in the pulp in a predominating capacity or which would be subsequently formed from materials originally present during the processing into viscose. These new materials are of the cation active class, which means that the group or groups responsible for surface activity is in the positive instead of the negative ion of the molecule. As a class, cation active substances are, as will be outlined, superior in a number of ways to the anion active class for use in the viscose process prior to xanthation especially as regards treatment of the original pulp. A great many cation active materials are soluble in all concentrations of caustic soda that would be encountered in any stage of the viscose process. This caustic soda solubility has certain advantages as regards the final viscose solution but would seem to preclude or limit their use to steps subsequent to steeping or to the use in the steeping caustic which would however be more expensive. It is at this point that we have made the unexpected and novel discovery that cation active materials possess the remarkable and important property of being adsorbed and held very firmly by cellulosic materials in the presence of steeping caustic soda solutions.

The closeness of the association and the firm-

ness with which the agent is held to the cellulose even in strong caustic soda solutions comprises a surprising and remarkable result. Thus, even though a cation active agent may be completely soluble in 18% caustic soda in the absence of cellulose, on the other hand when pulp is impregnated with such an agent and then steeped in 18% caustic soda, as in the first step of the viscose process, such material is substantially retained by the pulp due to the strong attraction for the cellulose.

Another great practical advantage in using cation active materials for treating the pulp itself results from the substantivity of these materials toward cellulose. Thus the pulp may be treated with these agents prior to sheet formation as for example in the form of a dilute suspension of pulp in water in a stock chest without the necessity of very completely recirculating the white water. This is in contrast to the practical limitations under which anion active materials would usually have to be used when being applied to the pulp. With anion active agents it is generally necessary to apply these after the sheet has been formed and the greater part of the water has been removed, or in the event of addition prior to sheet formation to provide for a system of almost complete recirculation of the white water to prevent excessive loss of the agents. The cation active materials on the other hand will be substantially exhausted from a very dilute solution by a suspension of pulp fibers and the materials will be substantially retained by the fibers during the mechanical dehydration pursuant to sheet formation.

Another advantage of using cation active materials is that many of these (of the quaternary ammonium class) due to their solubility in caustic soda solutions will when used to treat a highly refined pulp of low ether extract yield exceedingly clear viscose solutions. Such viscose solutions are considerably clearer than those obtained when using the types of anion active material which we have found suitable for treating the pulp itself.

Another advantage of using cation active materials is that certain compounds constituting a particular sub-class of these are in very minute amounts extremely efficient in aiding the preparation of very superior and extremely stable emulsions of mineral oil in viscose for delustered rayon.

Our experiments show that the agents of our discovery neither beneficially contribute to or interfere with the penetration or wetting of the pulp in the steeping step. In short, the improvement brought about by our agents does not relate primarily to the penetration or wetting of the pulp. For instance, if only portions of the pulp employed in the manufacture of the viscose solution are treated with our agents, nevertheless there is no appreciable lessening of the improvements resulting from the use of our agents as respects the subsequent steps. The agents of our invention or discovery need not be applied to each or every sheet of the pulp, but such agents may be applied to alternate sheets of said pulp or to only a portion of the pulp material being processed into viscose. Moreover, our agent or agents can be added after steeping, for example during the shredding operation and yet nearly the full benefits of our invention accrue as if our agents were added to the original pulp itself. However, there are advantages in adding our agents to the pulp, firstly as a matter of con-

venience and secondly, in that a very uniform distribution is assured.

If cation active materials or agents are added to the viscose solution as such, the said additions merely function to lower the surface tension of the spinning solution and provide better spinning conditions. We have discovered that the great advantages and improvements herein set forth accrue only provided such cation active materials or agents are added to the pulp or to the materials being processed prior to the completion of xanthation. If these materials are added after xanthation, a viscose product of improved characteristics, such as is obtained when the said reagents are added prior to the xanthation step, is not obtained.

It is noteworthy that the viscose of our invention is characterized by being particularly free from undissolved or partly dissolved fibers which greatly facilitates subsequent filtrations. We have found that any filtration improvements which may be obtained by subsequently adding surface active materials to the viscose itself rather than prior to xanthation are of a very low order as compared to results obtained by employing our agents prior to the completion of xanthation and that such improvements as may be obtained are only brought about by the use of very high concentrations of surface active materials.

The advantages and improvements which our invention produce in the various steps of the viscose process are as follows and it is to be understood that all conditions and temperatures normally employed in the preparation of viscose may be employed with the use of our agents.

1. *Steeping*.—In the steeping process the action of the caustic soda should be uniform and complete; otherwise there would be parts of the fibers improperly prepared for xanthation. This uniformity of penetration can be properly insured by mechanical means, i. e., by correct sheet structure and proper manipulation in the steeping operation. Our invention does not in any way relate to improved steeping properties of the sheet. The presence of our agents in the pulp in the concentrations employed by us during this steeping procedure does not to our knowledge affect the normal wetting and penetrating action of the caustic.

2. *Shredding*.—A principal object of shredding is comminution of the sheet structure in order to expose all portions of the fibers to the action of carbon bisulphide in the subsequent xanthating step. It is also important that this comminution can be brought about without excessive mechanical action on individual fibers and it is thus an advantage to have an alkali cellulose which will shred up readily. The pulps treated with our agents disintegrate much more easily and completely in the shredding operation. In other words, our agents we have discovered bring about a very positive opening up of the fibers over and above that which occurs when the pulp or alkali cellulose is not treated with our agents. This increased degree of comminution is evidenced by an increase in the volume of the shredded crumb. With unchanged time, this increase may amount to 25 percent. On the other hand shorter shredding times are possible, resulting in considerable saving in power as well as time. Examples of the decrease in apparent density of the shredded alkali cellulose produced by the addition of cation active agents when using refined chemical pulp (0.07% ether extract) are shown in Table I.

TABLE I

Effect of treatment of refined chemical pulp with cation active materials on the apparent density of the shredded alkali cellulose

Type of cation active material	Amount based on pulp and specific material	Apparent density of shredded alkali cell	
		Untreated	Treated
General class of quaternary compounds.	.05% lauryl trimethyl ammonium chloride.	.195	.175
	.02% lauryl trimethyl ammonium bromide.	.195	.190
	.05% lauryl trimethyl ammonium bromide.	.195	.165
	.05% lauryl dimethyl ethyl ammonium bromide.	.195	.170
	.05% lauryl triethyl ammonium bromide.	.197	.175
	.02% cetyl trimethyl ammonium bromide.	.195	.190
	.05% lauryl methyl morpholinium bromide.	.195	.165
	.02% lauryl methyl piperidinium bromide.	.195	.180
	.05% lauryl methyl piperidinium bromide.	.195	.165
	.05% lauryl dimethyl cyclohexyl ammonium bromide.	.195	.160
Special sub-class of quaternary compounds.			

It will be evident that the improvement in the comminution of the alkali cellulose resulting from our invention may be applied to other fields than that of viscose e. g. the preparation of cellulose ethers and cuprammonium solutions from pulp by processes using shredded alkali celluloses.

3. *Xanthation.*—The pulps treated with our agents xanthate much more completely and uniformly. This is probably due in part to improvements in the prior step of shredding, but as evidenced from our experiments, is also due in part to an actual improvement of the xanthation reaction itself. This improvement in the xanthation reaction is very probably brought about through a better penetration of the alkali cellulose particles by the carbon bisulphide.

The result of improved xanthation is that viscose can be obtained which is very largely free from undissolved fibers and partly dissolved fibers or gels. This is very advantageous in that when the viscose is subsequently filtered, filtration is much more rapid, the filters remain open for a much longer time, and the product obtained is more uniform and superior.

This result is of extreme importance, since it cannot be realized otherwise such as by merely using an unduly large excess of carbon bisulphide in the xanthation reaction. Such excesses not only alter the properties of the xanthated crumb in an undesirable manner but also alter the properties of the finished viscose solution, so that there is an interference with normal processing.

On the other hand our discovery includes the unexpected result in the xanthation reaction, that with the use of our agents it is also possible to use lesser amounts of carbon bisulphide than are normally employed in xanthating. The quantity of carbon bisulphide involved in producing viscose is fairly standard and accordingly it was very unexpected that our discovery or invention should result in producing viscose of satisfactory quality with a smaller amount of carbon bisulphide than heretofore has been found necessary to produce yarn of a given quality. This has the direct result of lessening the viscose ripening time, as well as a saving of chemicals—thus lessening the production cost.

It has been stated above that with the use of our agents it is possible to use lower amounts of carbon bisulphide than normally employed in xanthating and to thus shorten the ripening time. Under normal conditions the use of less carbon bisulphide also produces the same effect but the physical properties of the yarn are impaired in that lower elongations are obtained. If, however, the amount of carbon bisulphide is reduced in the presence of one of our agents, such a lowering of the elongation does not take place. This is an unexpected result. Another advantage of the use of smaller amounts of carbon bisulphide lies in the fact that the tendency toward undesirable milkiness in the rayon is materially minimized.

4. *Dissolving.*—The thoroughness and uniformity of the xanthation reaction when carried out with the use of surface active agents according to our invention is evidenced by the low number of partially reacted and unreacted fibers remaining after the xanthated product is dissolved in dilute caustic soda. Microscopic comparisons of normal viscose preparations with viscose prepared from refined chemical pulp (0.07% ether extract) using cation active agents according to our invention show very substantial reductions in undissolved and partly dissolved fibers as can be seen from Table II.

TABLE II

Effect of treatment of refined chemical pulp with cation active materials on the amount of undissolved and partially dissolved fibers in the viscose

Type of cation active material	Amount based on pulp and specific material	Total number of undissolved and partially dissolved fibres per c. c.	
		Untreated	Treated
General class of quaternary compounds.	.05% lauryl trimethyl ammonium bromide.	336	54
	.05% lauryl triethyl ammonium bromide.	336	60
	.05% lauryl dimethyl ethyl ammonium bromide.	336	156
	.05% lauryl methyl morpholinium bromide.	336	132
	.05% lauryl methyl piperidinium bromide.	336	120
	.05% lauryl dimethyl cyclohexyl ammonium bromide.	336	179
Special sub-class of quaternary compounds.			

5. *Filtration.*—Our invention remarkably facilitates the various filtration steps which the viscose undergoes subsequent to xanthation. This increase in filtration rate is due at least in part to a very substantial reduction in undissolved fibers and gels which are very effective in clogging the filtration medium. If the product is relatively free of undissolved or partially dissolved fibers or gels, the filter medium will continue unclogged for long periods eliminating frequent interruptions of the filtering process to permit the installation of fresh filtering media. This is obviously a distinct advantage.

Examples of the improvement in filtration brought about by our cation active agents over normally prepared viscose when using a refined chemical pulp (0.07% ether extract) are shown by the laboratory filtration data in Table III.

TABLE III

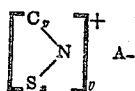
Effect of treatment of refined chemical pulp with cation active materials on the viscose filtration rate

Type of cation active material	Amount based on pulp and specific material	Viscose filtration rate (cc. per sq. cm. per hour)	
		Untreated	Treated
General class of quaternary compounds.	.05% lauryl trimethyl ammonium chloride.	527	620
	.02% lauryl trimethyl ammonium bromide.	527	730
	.05% lauryl trimethyl ammonium bromide.	527	680
	.05% lauryl dimethyl ethyl ammonium bromide.	527	650
	.05% lauryl triethyl ammonium bromide.	527	680
	.02% cetyl trimethyl ammonium bromide.	527	620
	.05% lauryl methyl morpholinium bromide.	527	755
	.025% lauryl pyridinium bromide.	527	670
	.05% lauryl pyridinium bromide.	527	828
	.02% lauryl methyl piperidinium bromide.	527	750
Special subclass of quaternary compounds.	.05% lauryl methyl piperidinium bromide.	527	920
	.05% lauryl dimethyl cyclohexyl ammonium bromide.	527	860

6. *Emulsification.*—In general the use of cation active agents according to our invention substantially improves the ease with which mineral oil may be dispersed in the viscose and the stability of emulsions thus formed in the production of delustered yarns. We have discovered, however, that a particular sub-class of the general cation active group gives extraordinary good emulsification results and that to produce these results only extremely small amounts of the materials are required (0.01 to 0.20% on the pulp—preferably 0.05 to 0.10%). This particular type of compound which has proven better in aiding the preparation of superior, stable emulsions than any other type used in comparable concentrations will be described in detail later.

As regards the general class of cation active materials which we have found provide improvement in the said various steps or operations in the preparation of the viscose, the most important of these can be grouped under the term, quaternary ammonium compounds. This refers to compounds having four organic groups linked to the nitrogen, (it being noted that a ring may count as either three or two groups) by the covalent type of bond produced by sharing of electrons. The fifth valence links an inconsequential negative group usually inorganic by an ionic-type bond. Such quaternary cation active compounds can be represented by the following general formula:

Formula I



The collection of groups in the bracket makes up the cation, while A is an inconsequential anion (such as bromide, chloride, iodide, sulphate, hydroxide, etc.) not imparting surface activity. S represents a group or groups (in the latter case, either similar or dissimilar) imparting surface activity. x represents the number of these groups. Such groups may be aliphatic chains of

greater magnitude than six carbon atoms and not to exceed twenty, the usual range being from eight to eighteen carbon atoms. Instead of aliphatic chains, we may have aromatic, cycloaliphatic or heterocyclic groups provided such groups are of sufficient molecular magnitude as to induce surface activity. C represents a group or groups which do not impart surface activity to the cation. These groups may be either of the chain or cyclic type and are in general of lesser molecular size than any similar type groups which would impart surface activity. The number of these groups (y) is such as to make the number of co-valent held groups four, or the total number of groups held by the nitrogen atom five. The letter v outside the bracket is equal to the valence of the inconsequential anion and hence also indicates the number of surface active cations in the molecule.

Examples of these quaternary ammonium surface active compounds are:

Lauryl pyridinium chloride
Lauryl trimethyl ammonium bromide
Lauryl trimethyl ammonium chloride
Lauryl dimethyl ethyl ammonium chloride
Lauryl triethyl ammonium bromide.
Cetyl trimethyl ammonium bromide
Lauryl methyl morpholinium bromide
Lauryl methyl piperidinium bromide
Lauryl dimethyl cyclohexyl ammonium bromide

In general, as has been stated, cation active materials when added to the pulp give improvements in the various stages of the viscose manufacture. Also, in addition, varying degrees of improvement in the emulsification of the viscose with mineral oil for the production of delustered rayon are obtained. We have made a further important discovery in that we find that we can prepare emulsions of mineral oil in viscose, characterized by extraordinary fineness of particle size and stability through use in the pulp of minute quantities of certain cation active materials which can be regarded as a sub-class of the general quaternary ammonium class. This important sub-class may be defined as those quaternary compounds which have linked to the nitrogen (a) one or more groups imparting surface activity comprising hydrocarbon chains of 7 to 20 carbon atoms, (b) one or more cyclo-aliphatic rings of which the nitrogen is either part or in close proximity and containing no heterocyclic atom other than a pentavalent nitrogen in the cases indicated and (c) small organic groups such as methyl in sufficient number as to give the nitrogen four co-valent and one ionic bonds. This may be represented by a general formula as below.

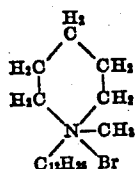
Formula II



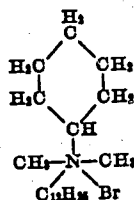
S represents a group or groups (in the latter case, either similar or dissimilar) imparting surface activity of the nature defined under (a) above. x represents the number of these groups. R is one or more cycloaliphatic rings of the type specified and z the number of these rings. If the nitrogen atom makes up part of a cyclo-aliphatic ring, two of the nitrogen's four co-valent bonds will be used up in this manner. C represents small organic groups such as methyl and in sufficient number as to account for the remaining valences of the nitrogen. There may be zero, or

one or more of these groups. The letter ν outside the bracket is equal to the valence of the inconsequential anion and hence also indicates the number of surface active cations in the molecule.

Two specific examples of materials of this class producing very remarkable emulsification results as well as improvements in the various steps in the preparation of the viscose are lauryl methyl piperidinium bromide, and lauryl dimethyl cyclohexyl ammonium bromide. It will be understood that the anion, in this case bromide, is not of consequence since it does not impart surface activity. Such anion could be chloride, iodide, sulphate, etc. Formulae representing these specific examples are:



Lauryl methyl piperidinium bromide



Lauryl dimethyl cyclohexyl ammonium bromide

It should be understood that by use of these specific agents according to our discovery not only is viscose produced which will emulsify exceedingly well with mineral oil but there are also obtained all the improvements in the various stages of the viscose manufacture given by the general class of cation active materials.

The effective range of the cation active compounds employed has been found by us to be from .01% to .20% said percentages being based on the weight of the bone dry pulp. With .01% some of the improvements of our invention begin to manifest themselves and this effect increases as the concentration is increased up to about .1%. Thereafter there seems to be little improvement, i. e., in filtration. There are disadvantages to using higher concentrations than .020% other than the matter of expense. As regards treatment of the pulp, such higher concentrations would cause excessive softness in the sheet resulting in mechanical difficulties in steeping. Furthermore, higher concentrations of the agents cause difficulties, in xanthation due to excessive ball formation, in dissolving due to excessive foaming and subsequently in de-aerating the viscose.

It will be understood that the use of cation active agents according to our invention is not subject to any limitations as to the methods of application other than that the materials be added prior to the completion of xanthation. Practical methods for carrying out the invention include both treatment of the pulp prior to use in the viscose process and the introduction of the agents at some point during the processing of the pulp into viscose prior to the completion of xanthation. In the latter case, for example, the agents may be sprayed into the shredder prior to the completion of shredding or they may be dissolved in the steeping caustic solution.

As the regards treatment of the pulp with the agents of our discovery prior to use in the viscose process, examples of practical methods of treatment follow though it is to be understood that our invention is not limited to any specific method of application. A suitable point in pulp manufacture for treatment with cation active agents is the addition to the pulp on the machine subsequent to sheet formation but prior to drying. The agents can be suitably added from aqueous solutions either by means of sprays or by means of a rotating roll partly immersed in the treating solution.

Also, as has been stated, with cation active agents it is very practical to treat the pulp in suspension prior to sheet formation. Owing to the substantive nature of these materials toward cellulose, they will be largely exhausted from a dilute solution on to the fibers and will be substantially retained during the removal of the large proportion of water in sheet formation. It is thus not necessary to provide a system for very completely recirculating the white water on the machine without diversion to other points in the plant to avoid excessive loss of the agents and the interference with other portions of the process.

We claim:

1. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation a lauryl methyl piperidinium compound having an anion not inducing surface activity, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

2. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation a lauryl dimethyl cyclohexyl ammonium compound having an anion not inducing surface activity, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

3. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation lauryl methyl piperidinium bromide in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

4. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation lauryl dimethyl cyclohexyl ammonium bromide in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

5. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to the pulp prior to use lauryl methyl piperidinium bromide in a concentration ranging from 0.01% to 0.20% by weight, such per-

centages being based on the weight of the bone dry pulp.

6. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to the pulp prior to use lauryl dimethyl cyclohexyl ammonium bromide in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

7. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation a surface active quaternary ammonium compound at least dispersible in solutions of alkali metal hydroxide consisting of a piperidinium compound wherein one of the groups attached to the pentavalent nitrogen is an aliphatic hydrocarbon chain of 7 to 20 carbon atoms, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentage being based on the weight of the bone dry pulp.

8. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation a surface active quaternary ammonium compound at least dispersible in solutions of alkali metal hydroxide consisting of a cyclohexyl ammonium compound wherein one of the groups attached to the pentavalent nitrogen is an aliphatic hydrocarbon chain of 7 to 20 carbon atoms, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentage being based on the weight of the bone dry pulp.

9. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to such refined chemical pulp prior to use in the viscose process a cation active quaternary ammonium compound at least dispersible in, and whose cation is stable in, solutions of alkali metal hydroxide, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

10. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation, a cation active quaternary ammonium compound at least dispersible in solutions of alkali metal hydroxide and wherein at least one of the groups attached to the pentavalent nitrogen is an aliphatic hydrocarbon chain of 7 to 20 carbon atoms, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the bone dry weight of the pulp.

11. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose comprising adding to such refined chemical pulp prior to use in the viscose process a cation active quaternary ammonium compound at least dispersible in solutions of alkali metal hydroxide and wherein at least one of the groups attached to the pentavalent nitrogen is an aliphatic hydrocarbon chain of 7 to 20 carbon atoms, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the bone dry weight of the pulp.

12. The method of improving the manufacture of shredded alkali cellulose from refined chemical pulp containing not more than 0.15% ether extractable matter comprising adding to one of the alkali cellulose forming materials at a stage prior to completion of shredding a cation active quaternary ammonium compound at least dispersible in, and whose cation is stable in, solutions of alkali metal hydroxide, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

13. As a new article of manufacture, a refined chemical pulp product containing not more than 0.15% of natural ether extractable matter and having incorporated therein a cation active quaternary ammonium compound at least dispersible in, and whose cation is stable in, solutions of alkali metal hydroxide, the amount of the incorporated quaternary ammonium compound being from 0.01% to 0.20% by weight, such percentages being based on the bone dry weight of the pulp.

14. As a new article of manufacture, a refined chemical pulp product containing not more than 0.15% of natural ether extractable matter and having incorporated therein a surface active quaternary ammonium compound at least dispersible in solutions of alkali metal hydroxide and consisting of a piperidinium compound wherein one of the groups attached to the pentavalent nitrogen is an aliphatic hydrocarbon chain of 7 to 20 carbon atoms, the amount of the incorporated quaternary ammonium compound being from 0.01% to 0.20% by weight, such percentages being based on the bone dry weight of the pulp.

15. The method of improving the processing of refined chemical pulp containing not more than 0.15% ether extractable matter into viscose, comprising adding to one of the viscose forming materials at a stage prior to completion of xanthation a cation active quaternary ammonium compound at least dispersible in, and whose cation is stable in, solutions of alkali metal hydroxide, said compound being added in a concentration ranging from 0.01% to 0.20% by weight, such percentages being based on the weight of the bone dry pulp.

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