

UNITED STATES PATENT OFFICE

2,481,692

COTTON TREATED WITH A CATION
ACTIVE AMINE

Paul Henry Schlosser and Kenneth Russell Gray,
Shelton, Wash., assignors to Rayonier Incorporated,
Shelton, Wash., a corporation of Delaware

No Drawing. Application April 12, 1944,
Serial No. 530,740

5 Claims. (Cl. 106—165)

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This invention relates to the production of cellulosic products and has for its object the provision of certain improvements in the production of cellulosic products from cotton, and particularly cotton linters. The invention is of special advantage in the production of regenerated cellulose products, and particularly by the viscose process, from cotton. A further object of the invention is the provision, as a new article of manufacture, of an improved cellulosic product consisting mainly of cotton.

Cotton, and more particularly cotton linters, is extensively used in the production of various cellulosic products such, for example, as nitrocellulose, cellulose acetate, cellulose ethers, rayon and other synthetic fibers, cellophane and similar cellulosic films or sheets, etc. Cotton is available as a source of cellulose in the raw state and as chemical cotton in loose form or in sheet form. In neither case is the cotton subjected to any textile operation to form it into threads or fabric; and in the appended claims the term "cotton in the raw state" is used to designate raw cotton or raw cotton which has been subjected to chemical treatment to purify and bleach it, as hereinafter referred to, but which has not been subjected to any textile operation to form it into threads or fabric. The invention aims to incorporate in such cotton, or its derivatives, one or more added compounds of the invention to improve one or more of the steps in the formation of the cellulosic products.

Chemical cotton in sheet form is customarily subjected to comminution or shredding as one of the preliminary steps in its processing. In the production of viscose, for example, the sheets formed of cotton linters are usually steeped in a caustic soda solution to form alkali cellulose and the alkali cellulose, after pressing and while still in sheet form, is shredded to prepare the cotton 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, opacified if desired, is filtered and spun into filaments.

We have discovered that the incorporation in cotton, advantageously in cotton linters, of certain compounds in minute quantities, imparts to the cellulose, properties that make it more amenable to various processing steps in the production of rayon by the viscose process, resulting in increased efficiency and a decrease in the cost of the operation. The invention accordingly involves the incorporation in the cotton of a small quantity of a cation-active amino compound and

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the utilization of the cotton so treated for the production of viscose rayon. The invention provides as an article of manufacture an improved product comprising cotton, especially cotton linters, having one or more of said compounds incorporated therein.

In practices proposed heretofore, cation-active compounds as strong bases or their salts including quaternary ammonium, sulphonium, phosphonium and arsonium salts have been used in the spin bath to reduce incrustations in the spinneret orifices. When added to the viscose, such compounds also reduce incrustations in spinneret orifices, though in general considerably larger concentrations are required to be present and such additions will frequently cause certain disadvantages as will be presently set forth.

We have made the discovery that important new advantages accrue if there is caused to be present in the viscose, in a manner as will be specified, compounds which have only a weakly cation-active behavior while in the viscose, but which becomes strongly cation-active at the point of spinning. For such purposes, we find that cation-active amino compounds are eminently suitable.

The cation-active amino compounds or agents of the invention when used in the manner of the invention yield all of the advantages hitherto obtainable only by use of larger amounts of quaternary ammonium compounds. In addition, the agents of our invention yield important new advantages and are free or largely free from the disadvantages accompanying the use in viscose of highly ionized cation-active materials such as cation-active quaternary ammonium compounds.

Cation-active amino compounds in alkaline solution derive their attraction for water from one or more weakly hydrophilic amino groups rather than from strongly hydrophilic groups as in the case of quaternary ammonium compounds. Accordingly, in many cases cation-active amino compounds will not be clearly soluble in caustic soda solutions, but will disperse rather than dissolve. It would be thought that it would be disadvantageous to use materials that would disperse rather than dissolve in viscose. Actually, if such materials which tend to disperse rather than completely dissolve are added directly to the viscose, they will be only partially effective due to incompleteness of the dispersion. Also, with the more difficulty dispersible cation-active amino compounds, when added directly to the viscose the incompleteness of dispersion may be such that considerable of the agent may be

removed during the customary viscose filtration operations with the result that the filtering media may become rapidly clogged, requiring frequent replacement. These difficulties are not encountered when the agents are added in the manner of the invention—by impregnating the cellulose base material, preferably cotton linters, with the agents prior to use in the viscose process. The impregnation is preferably carried out by use of an aqueous solution or dispersion of the agent, best in the form of a soluble salt such as the acetate. When the cellulosic base material is treated with the agent in this manner, the agents of the invention become dispersed in the viscose in a very fine state so that they are very effective in accomplishing the purposes of the invention.

All purified cellulose base materials commonly used for the preparation of viscose rayon contain varying amounts of anion-active materials or of materials which will give rise to anion-active materials when in contact with caustic soda during the various steps of the viscose process. Such anion-active materials will be predominantly fatty and resin acid soaps. Cotton linters will generally contain appreciably smaller amounts of such soap-forming materials than will most purified wood pulps. Cotton linters, however, when used for viscose rayon, are frequently blended with purified wood pulps in order to improve spinning and other processing conditions. In such cases, the resulting viscose solutions will contain appreciable amounts of anion-active materials and may contain additional amounts if the wood pulp has been treated in accordance with United States Patent 2,331,935.

Also, when cotton linters are used in the viscose process, relatively large amounts of anion-active materials are frequently added to the viscose or the viscose-forming materials to reduce milkiness in the rayon or to otherwise improve the spinning operations. Such additions of anion-active materials are made frequently in the cases where the cotton linters are not mixed with purified wood pulp prior to processing. Thus, whether the cotton is processed alone or in admixture with wood pulp, the resulting solutions will, in most cases, contain appreciable amounts of anion-active materials.

Cation-active quaternary ammonium compounds, while very useful for suppressing formation of incrustations in spinneret holes, nevertheless, when introduced into the viscose rather than the spin bath possess a considerable disadvantage in that they are not very compatible with anion-active materials. If cation-active quaternary ammonium compounds are introduced into viscose in which there happens to be present an approximately equivalent amount of anion-active materials, an actual precipitation of materials may occur in the viscose or at the very least the viscose may become very turbid. Such precipitated material is likely to plug the filters and cause spinning troubles.

Even when the relative proportions of cation-active quaternary ammonium compounds and anion-active materials are such that actual precipitation does not occur, troubles may still be encountered through simultaneous use of the two types of materials. Such troubles are particularly encountered when the anion-active materials are present in sufficient quantity to predominate over the quaternary ammonium compounds and this viscose is opacified by oleaginous materials such as mineral oil, or pine oil or by

means of opacifying agents containing oleaginous materials. In general, where a cation-active quaternary ammonium compound is added in amounts insufficient to predominate over anion-active materials present, the effect is to make the emulsion poorer than if only the anion-active materials had been present. In such cases the effect of the cation-active quaternary ammonium compound will be to cause a greater lack of uniformity of the emulsion in regard to particle size and in particular to bring about the presence of numerous globules considerably larger than the average particle size. Such large globules even when relatively few in quantity are very harmful in that they cause irregularities in the viscose filaments and resulting places of weakness. In some cases when cation-active quaternary ammonium compounds are used in the presence of predominating amounts of anion-active materials the interference with the emulsification or with the stability of the emulsions may be such that large visible drops or pools of oil will separate and float on top of the emulsion. One way of overcoming such difficulties might be to use very large amounts of the cation-active quaternary ammonium compounds so that they would substantially predominate over the anion-active materials present. This would be very expensive since cation-active quaternary ammonium compounds are much more expensive than commonly used anion-active materials. However, the additions of very high amounts of cation-active quaternary ammonium compounds are accompanied by serious disadvantages other than as regards the matter of expense. In making high grade rayon it is essential that all foreign materials or impurities be eliminated and therefore the adding of very large amounts of cation-active quaternary ammonium compounds is proceeding directly against the requirement of the elimination from the cellulosic base material of all materials other than the cellulose itself. Again, the use of very large amounts of cation-active quaternary ammonium compounds will tend to cause certain disadvantages which include (a) excessive roaming when mixing the viscoses; (b) difficulties in subsequently deaerating the viscose, and (c) difficulties in spinning due to the very low surface tension of the viscose.

The agents of our invention, however, are much more compatible with anion-active materials than are cation-active quaternary ammonium compounds. Their use in viscose is therefore not accompanied by the disadvantages of the cation-active quaternary ammonium compounds.

The agents of our invention moreover are more effective in that they can be used in much smaller concentrations, even in the presence of anion-active materials. The agents of our invention also produce new advantages. Not only is the process of our invention inexpensive to operate in that only very small quantities of the agents are required but, moreover, the agents themselves are in general considerably less expensive than the previously used types of cation-active compounds. The cation-active amino compounds in general may be very inexpensively produced from the natural fats and other readily available raw materials.

Not only are the cation-active agents of our invention compatible with the anion-active compounds that will be commonly present in viscose solutions (either naturally or by addition) but the agents of our invention actually improve the emulsifying action of the anion-active com-

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pounds. This improvement relates particularly to the imparting of stability against creaming of emulsions prepared using oleaginous opacifying agents and viscose containing anion-active emulsifying agents; e. g., fatty and resin acid soaps.

Many anion-active emulsifying agents while not yielding emulsions of oil in viscose having as fine average particle size and uniformity as those specified in United States Patent No. 2,373,712, nevertheless are relatively inexpensive and yield emulsions that will be satisfactory for many purposes with reference to particle size and stability in regard to maintaining particle size. Such emulsions, however, have a tendency to cream partially or for part of the oil to separate out as a scum during the various viscose processing steps or during the aging period. We find that the addition of very small amounts of the cation-active agents of our invention either eliminates or greatly diminishes the tendency of the emulsions to cream. While all the agents of our discovery are effective in this regard, the best results are obtained by the more dispersible cation-active amino compounds, usually compounds containing a plurality of amino groups. Thus octadecylamine (acetate) has an extremely small anti-creaming effect. Dodecylamine or the mixture of normal primary amines from coconut fatty acids have a greater but still small anti-creaming action. Materials, however, such as mixtures of the mono- and diamides of coconut fatty acids and diethylene triamine, which are very readily dispersible, exert a very powerful emulsion anti-creaming effect even when added in very small quantities.

When even those cation-active amino compounds having the greatest anti-creaming action are added directly to the viscose either prior or during emulsification, very little reduction in creaming is obtained. When, however, these agents are added to the alkali cellulose prior to the completion of shredding or preferably to the cellulose base material prior to use in the viscose process, complete or substantial reduction in creaming is obtained.

Especially good emulsification results are obtained when there is added to the cotton linters in addition to the small amounts of cation-active amino compounds, also small amounts of a mixed ether containing a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms. The very best results occur when the said mixed ether contains a polyethylene oxide radical of 9 to 20 ethenoxy residues and a normal aliphatic hydrocarbon radical having from 12 to 18 carbon atoms. Such emulsions not only are characterized by a high degree of non-creaming stability but also are characterized by an extremely fine and uniform particle size with almost complete absence of substantially larger globules. The emulsions are also very stable in regard to maintaining the fineness and uniformity of the particle size.

In addition to the advantages already outlined, the use of the agents of our invention also gives a very great general improvement in spinning performance. By this improvement we refer to benefits apart from that brought about by obtaining less incrustation of spinneret holes. These general improvements include especially improvements in coagulation of the cellulose resulting in less sticking of the freshly formed yarn to the spinning guides and fewer broken filaments. This is of the utmost practical importance

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since it enables substantially reducing the proportion of off grade yarn produced.

Amino groups are of three types: Primary, secondary and tertiary. Each of these types may exist in five different forms to a different degree (in some cases completely and in others to only a small degree):

1. Free amino group—anhydrous.
2. Free amino group—hydrated and not ionized.
3. Free amino group—hydrated and ionized.
4. Amino group in form of salts with acids—non-ionized.
5. Amino group in form of salts with acids—ionized.

The three types in their different forms may be shown as follows:

Form	Type I Primary Amino Group	Type II Secondary Amino Group	Type III Tertiary Amino Group
1-----	$-\text{NH}_2$	>NH	>N
2-----	$-\text{NH}_2\text{OH}$	$\text{>NH}_2\text{OH}$	>NHOH
3-----	$[-\text{NH}_2]^+\text{OH}^-$	$[\text{>NH}_2]^+\text{OH}^-$	$[\text{>N}]^+\text{OH}^-$
4-----	$-\text{NH}_2\text{X}$	$\text{>NH}_2\text{X}$	>NHX
5-----	$[-\text{NH}_2]^+\text{X}^-$	$[\text{>NH}_2]^+\text{X}^-$	$[\text{>N}]^+\text{X}^-$

In the table above the free bonds shown represent carbon-nitrogen linkages, while the symbol "X" represents the anion of an acid forming a salt with the free amino group.

Generally in the presence of water, an amino group in the form of a salt (substituted ammonium salt) will be largely in the ionized form. In the presence of water (except in very dilute solutions), compounds containing one free amino group, however, will exist largely in the non-ionized forms, hydrated and anhydrous. Obviously, with compounds containing a multiplicity of free amino groups in the presence of water as in viscose solutions, there will be a greater proportion of molecules having at least one amino group in the hydrated, ionized form. However, even in such cases, the percentage of ionized molecules will be extremely small so that the compounds will be only extremely weakly ionized; i. e., only very weakly basic and, hence, though surface-active, only weakly cation-active.

As used generically in this application, the term "amino compound" refers to a compound having at least one of any of the three types of amino groups shown in the table in any one, or in an equilibrium mixture of more than one, of the five forms shown.

Surface-active compounds are compounds containing one or more lipophilic (oil or fat attracting, water repulsing) groups together with a hydrophilic group or a plurality of hydrophilic groups. Further, the lipophilic group or groups must be of sufficient magnitude to impart to a portion of the molecule a substantial repulsive action towards water. The hydrophilic group or plurality of hydrophilic groups must possess a sufficient hydrophilic character so that the molecule is water-soluble or at least soluble to the ex-

tent that it is readily dispersible in a finely divided form in water.

The surface-active property of molecules thus arises as the result of their containing at least one hydrophilic (water attracting) group and at least one lipophilic (fat or oil attracting and hence water repulsing) group. By virtue of the compounds containing a hydrophilic group, they are at least to a certain extent soluble in water. However, by virtue of their containing a lipophilic group, they tend to be repulsed by the water. Thus they tend to concentrate largely on the surface of the water or interface layer where they can take up a compromise position with the hydrophilic group resting in the water and the lipophilic group sticking out of the water.

The compounds of the invention are such surface-active lipophilic-hydrophilic combinations in which the hydrophilic effect is provided either wholly or in part through the presence of an amino group or a plurality of amino groups. That the compounds are "cation"-active is due to the fact that they will ionize either largely through the form of their salts with acids or to a small extent through the form of a hydrated free amino group.

Where the compounds contain a plurality of amino groups, these are preferably connected by short links—for example, by ethylene groups or by segments of a ring, though longer connecting links are not ruled out.

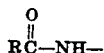
Many of the compounds of the cation-active amino class while soluble and definitely cation-active in the form of their salts with acids are, nevertheless, neither soluble nor readily dispersible in strong caustic soda solutions. Such materials, when added as a solution in salt form, to a solution containing excess alkali, separate out almost completely in the form of oils or solid precipitates. Due to the lack of solubility or dispersibility in an alkaline medium, such compounds might possibly not normally be considered to be effective in alkaline solutions. When, however, they are added to the cotton in the form of soluble salts, they subsequently disperse in the viscose and are effective in the process of the invention.

While the compounds of the invention are not necessarily dispersible or soluble in the free base form, the free bases must, nevertheless, be substantially stable in solutions of alkali metal hydroxide.

Where the compounds are employed as salts, the salts of any acid whose anion would normally be innocuous in small concentrations to the viscose process may be used. Such innocuous anions include acetate, chloride, sulphate, etc. We believe in many cases best results will be obtained with the acetates. These salts are less acidic than similar salts of mineral acids and are thus preferred when treating the cotton linters. Also with those amino compounds of the invention that tend to form difficultly soluble salts, the acetates are frequently more soluble or dispersible than the salts of mineral acids.

In the compounds of the invention the lipophilic group (or each of the lipophilic groups) has substantially a hydrocarbon character but is not limited to hydrocarbon radicals.

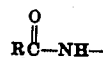
Among the important lipophilic groups are the radicals R,



and R—O— where R is a higher aliphatic hydro-

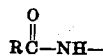
carbon radical. These radicals may be derived from fats, waxes, vegetable oils, mineral oils, etc. The aliphatic hydrocarbon radicals represented by R include straight chain, branched chain, saturated and unsaturated radicals. Other groups such as cyclic hydrocarbon groups or groups containing a small proportion of other elements than carbon and hydrogen are, however, not excluded.

A lipophilic aliphatic hydrocarbon radical (R) may be connected directly to the amino group (or to one of the plurality of amino groups). The lipophilic groups

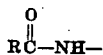


and R—O— are, however, always connected to the nitrogen through stable intermediary links—preferably, though not restricted to, short alkylene groups such as the ethylene group (—CH₂CH₂—).

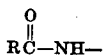
In regard to the use of the lipophilic groups R,



and R—O— to induce surface activity, suitable groups will include those having at least 7 carbon atoms. There is a practical upper limit for these or any other type of lipophilic surface-active inducing radical in that the compounds must be soluble or at least dispersible in water in the form of salts, if not also as the free base. In the preferred cases the group R,



or R—O— will have from 7 to 18 carbon atoms. Especially good results have been obtained from compounds in which the radicals R,



or R—O— had 12 carbon atoms or were prepared from a vegetable oil, such as coconut oil, predominating in lauric acid so that the resulting radicals were mixtures having predominately 12 carbon atoms.

Among the types and individual examples of cation-active amino compounds which may be used are the following:

1. ALKYL AMINES

a. Primary alkyl amines

Primary amines, saturated and unsaturated, straight chain and branched chain with from 7 to 18 carbon atoms are effective. In view of the fact that the free bases are not readily dispersible in water by normal procedures and, in view of the fact that the lower free bases are somewhat volatile, these compounds are most practically applied to the cotton as solutions of water-soluble salts, in most cases preferably as the acetates. Some members can, however, be fairly readily dispersed in water by using special procedures, as, for example, by dispersing the alkyl amine in the presence of a small amount of a soluble salt of the amine.

Among the members of this series that we have successfully used are the following:

Heptyl amine, octyl amine, (2-ethyl) hexylamine-1 decylamine, lauryl amine, tetradecylamine, hexadecyl amine, oleylamine, octadecylamine. We have found the most effective and practical compound to apply to be lauryl amine. Actually the technical mixture of primary amines derived from coconut oil and predominating in lauryl amine works very well—slightly better than the pure compound.

The higher members, e. g., octadecylamine, form salts that are only slightly water-soluble, and while giving the advantages of the invention in part, are more difficult to apply in a practical manner.

b. Secondary and tertiary alkyl amines

The members of these series will all contain at least 7 carbon atoms. In all cases the upper limit of carbon atoms will be such that the compounds will form salts that are appreciably water-soluble. The most preferred types will contain one long chain while the other chain or chains will be very short, preferably (though not restricted to) methyl or ethyl groups. Examples are methyl lauryl amine, dimethyl lauryl amine.

These compounds are likewise best applied in the form of water-soluble salts.

2. ALKYL ALKANOLAMINES (ALKYL HYDROXYALKYLAMINES)

While compounds of this type may be readily applied in the form of soluble salts, many compounds of this type are sufficiently dispersible in water in free base form to be used as such.

Examples of compounds successfully used include lauryl amino-ethanol (lauryl hydroxyethyl amine), condensation products of lauryl amine and glycerine chlorohydrin, N-bis (2-ethyl hexyl) amino ethanol.

3. ALKYL ETHERS OF ALKANOLAMINES (ALKYL ETHERS OF HYDROXYALKYLAMINES)

We have used the lauryl ether of ethanolamine (in salt form), the monolauryl ether of triethanolamine (in salt form).

4. ALKYL CYCLOALKYL AMINES

Compounds of this type are best applied in the form of water-soluble salts. Examples are lauryl piperidine, lauryl methyl cyclohexylamine.

5. AMIDO AMINES

a. Monoamides of hydroxyethyl polyethylene polyamines

Compounds of this type may be applied in the form of water-soluble salts but many are sufficiently water-dispersible or soluble to be applied in free base form. Suitable hydroxyethyl polyethylene polyamines for use in preparing the compounds include hydroxyethyl ethylene diamine and hydroxyethyl triethylene tetramine. The preferred amido amine compounds of this type are condensation products which are predominantly monoamides of hydroxyethyl ethylene diamine and fatty acids having from 7 to 18 carbon atoms.

Examples of compounds successfully used are the monoamides of hydroxyethyl ethylene diamine and oleic, stearic, and mixed coconut fatty acids (the latter predominating in lauric acid). The compound derived from a coconut fatty acids is very effective.

b. Partially acylated polyethylene polyamines

Polyethylene polyamines that we have successfully used in preparing compounds of this type include diethylene triamine, triethylene tetramine and tetraethylene pentamine. The preferred products are polyethylene polyamines partially acylated with a fatty acid of from 7 to 18 carbon atoms.

Practically, it is not feasible to prepare a substantially pure monoamide from these polyamines

containing 2 primary amino groups, since a substantial amount of diamide will always tend to form in addition to much smaller amounts of more completely acylated products. We prefer, however, to have the monoamide predominate or at least be as high as practically possible in any mixture of the two, in order that the material will be more water-soluble or dispersible and more effective. This will be especially true when the products are formed from the lower members of the polyamines. An increase in the proportion of monoamide can be accomplished in their preparation by using an excess of the polyamine over the fatty acid, or even better by using an excess of polyamine together with the ethyl or methyl esters of the fatty acids. In either case the excess amine may be substantially removed by vacuum distillation at the end of the reaction.

Examples of products of this type which we have successfully used in the practice of our invention include products having as the predominating compounds the following: Mixtures of the mono and diamides of tetraethylene pentamine and the fatty acids derived from coconut oil, mixtures of the mono and diamides of triethylene tetramine and the fatty acids derived from coconut oil, the diamide of triethylene tetramine and the fatty acids derived from coconut oil, mixtures of the mono and diamides of diethylene triamine and oleic acid, mixtures of the mono and diamides of diethylene triamine and stearic acid, mixtures of the mono and diamides of diethylene triamine and myristic acid, mixtures of the mono and diamides of diethylene triamine and mixed caprylic and capric acids.

Compounds of this type may be applied as solutions of soluble salts (acetates preferred) but in many cases are sufficiently dispersible in free base form to be applied to the cotton in that condition. Since the products are not pure compounds, in certain cases (as with hydrochlorides of certain products from diethylene triamine) solutions of the salts will contain in dispersed form a certain amount of undissolved matter. This, however, does not substantially harm the effectiveness of the products in the viscose process.

Having regard to both the effectiveness of the agents and the practical economics of their preparation, products which are predominantly a mixture of the mono and diamides of diethylene triamine and fatty acids from coconut oil, or other vegetable oil, predominating in lauric acid are very effective. Using coconut fatty acids with a mean molecular weight of 212, a monoamide of diethylene triamine would theoretically have a nitrogen content of about 14.15%, while a diamide would have a nitrogen content of about 8.55%. Among the products we have prepared and successfully used, and which are predominantly mixtures of mono and diamides, are products having the following nitrogen contents: 8.90%, 9.08%, 9.19%, 10.22%, 10.69%, 11.20%, 11.33%, 11.40%, 11.65%, 12.11%, and 12.97%. We most usually, however, employ products having nitrogen contents of around 11.2-11.7% (on an anhydrous basis).

c. Monoamides of derivatives of ethylene diamine

Compounds of this type are best applied as solutions of soluble salts. An example of a compound successfully used is the oleic acid amide of unsymmetrical diethyl ethylene diamine.

In addition to the amido amines described above under (a), (b) and (c) analogous amidines in

which the CO groups are replaced by C=NH groups may be used.

6. IMIDAZOLINES

Compounds of this type are best applied in the form of soluble salts. In the preferred cases they will have substituted in the ring an alkyl chain (saturated or unsaturated) of from 7 to 18 carbon atoms. Compounds successfully used include 2-undecyl imidazoline, 2-heptadecyl-N-acetamidoethyl imidazoline.

7. ALKYL GUANIDINES AND BIGUANIDINES

Suitable compounds of this type include guanidine and biguanidine monalkylated with an alkyl group of from 7 to 18 carbon atoms. A preferred compound is lauryl guanidine. These compounds are best applied in the form of soluble salts.

A preferred form of the invention contemplates incorporating in cotton linters a cation-active amino compound of the amido amine type. Cation-active amido amines are readily available and may in general be produced far more inexpensively than other types of cation-active materials. This is because their preparation merely involves heating common fatty acids or fats with low molecular weight polyamines whereby the carboxyl group is blocked by amidation but whereby free amino groups remain. Such compounds, however, are completely hydrolyzed by prolonged treatment with hot mineral acids. It would thus not be practical to add such compounds to a circulating spin bath to improve spinning. The large volume of the spin bath would necessitate the use of a large amount of the amido amine, most of which would become hydrolyzed before coming in contact with the spinnerets.

On the other hand, if such materials were added directly to the viscose there would in most cases be the problem of obtaining satisfactory distribution. Cation-active amido amines are most commonly provided in the form of soluble salts (such as acetates or sulphates). Since there are salts of very weak bases they cannot exist in alkaline solution, as for example, in viscose solution. When added directly to viscose, either as a dispersion of the free base or as a solution of a soluble salt, such compounds generally either disperse incompletely or partially precipitate. When, however, these compounds are added in the manner of the invention to cotton linters before processing into viscose (using either a solution of a soluble salt or a dispersion of the free base), none of these disadvantages ensue. Not only is a very complete distribution in the viscose obtained but the compounds only come in contact with the hot acid at the very moment of spinning with the result that no measurable amount of the compound is destroyed before it can become effective in improving spinning. Not only does the method of our invention thus permit the use of relatively inexpensive materials but these compounds also may be used in smaller amounts since they are more effective in improving spinning than compounds previously employed, such as cation-active quaternary ammonium compounds.

In accordance with our invention, we may mix two or more of the aforementioned compounds together to obtain effects not attainable with a single compound under similar conditions of treatment. For example, we may use a mixture comprising a cation-active amino compound, es-

pecially a cation-active amido amine and a mixed ether having attached to the ether oxygen a polyethylene oxide radical and an aliphatic hydrocarbon radical having from 7 to 18 carbon atoms. Such mixtures are especially efficacious in the method of our invention in improving spinning, enabling the production of yarn of superior quality and also in enabling the production of emulsions of oils in viscose characterized by extreme fineness, uniformity and stability.

Our invention also contemplates the manufacture of cotton linters containing a cation-active amino compound, especially one containing a plurality of nitrogen atoms (as, for example, an amido amine from diethylene triamine and coconut fatty acids) together with a small amount of anion-active material or anion-active forming material especially fatty or resin acid soaps or of materials capable of forming such materials in the presence of caustic soda. The cotton linters may or may not contain in addition a small amount of a mixed ether of the types described above.

A practical and economical manner of securing the desired presence of a compound of our invention during the step of spinning the viscose and during the step of opacifying the viscose if an opacifying step is employed is to incorporate the compound in the cotton using either a solution, dispersion or emulsion of the salt or free base, depending upon the compound. Chemical cotton is subjected to a purification and bleaching treatment. The purified and bleached cotton in slush form is then formed into sheets on a paper machine of conventional design. The sheet is passed over drying rolls and then cut into sheets of the desired size.

The compounds may be incorporated either in the loose cotton or in the sheets at any suitable stage, as by spraying the cotton with an aqueous solution or dispersion of the compound, or by immersing in a solution or dispersion. In any case, there is produced a cotton product having the compound incorporated therein. When the compound is incorporated in the cotton, as by the manufacture thereof, the cotton comes to the rayon manufacturer in a form calculated to secure the full advantages of the invention in the preparation and processing of the cotton into rayon by the viscose process.

The amount of the cation-active amino compound used in the practice of the invention is relatively small, ranging from 0.01 to 0.20%, and preferably from 0.02 to 0.10% by weight on the bone dry weight of the cotton used. So far as the objectives of the invention are concerned, there is little, if any, improvement by increasing the amount of the compound above 0.20% and such higher amounts frequently give rise to certain disadvantages. These disadvantages include the causing of excessive softness in the sheet, resulting in mechanical difficulties in steeping, difficulties in the dissolving due to excessive foaming in the viscose solution. Also, there may be considerable difficulty in obtaining a completely deaerated viscose which is necessary for satisfactory spinning. Higher concentrations of the compound may 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.

Where the said mixed ethers are also added

these may be added in amounts up to 0.20% but in most cases for best results will be added in the range of 0.02-0.05%. An example of a very efficacious combination would be about 0.05% of a mixture of amido amines from coconut fatty acids and diethylene triamine together with about 0.03% of a condensation product from a higher aliphatic alcohol of from 12-18 carbon atoms (either straight or branched chain), and about 5-18 moles of ethylene oxide.

While it is our preferred practice to incorporate the compound in the cotton, the presence of the compound during the processing steps of spinning and emulsification may be secured in any other appropriate manner. However, we believe it will generally be found more advantageous to incorporate the compounds in the cotton, both as a matter of convenience and economy in preparing and processing the viscose, and because a very uniform distribution of the compounds throughout the viscose is easily attained. Similar advantages result by incorporating the compound, especially the more dispersible compounds, in the alkali cellulose. The incorporation of the compound in the cotton or in the alkali cellulose is particularly important in regard to importing anti-creaming properties, especially if the viscose is to be subsequently opacified.

We claim:

1. As a new article of manufacture, a cellulosic product consisting of cotton in the raw state as a raw material for conversion into rayon having incorporated therein from 0.01% to 0.2% by weight, based on the bone dry weight of the cotton, of an added cation-active amino compound selected from the group consisting of an alkyl amine having from 7 to 18 carbon atoms, an alkyl alkanolamine having at least one alkyl radical having from 8 to 14 carbon atoms and having from 14 to 18 total carbon atoms, a lauryl ether of an alkanolamine, lauryl piperidine, lauryl methyl cyclohexylamine, an acylated polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an acylated hydroxyethyl polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an alkyl imidazoline having an alkyl radical having from 7 to 18 carbon atoms and an alkyl guanidine having an alkyl radical having from 7 to 18 carbon atoms.

2. As a new article of manufacture, a cellulosic product consisting of cotton in the raw state as a raw material for conversion into rayon having incorporated therein from 0.01% to 0.2% by weight, based on the bone dry weight of the cotton, of an added cation-active amino compound selected from the group consisting of an alkyl amine having from 7 to 18 carbon atoms, an alkyl alkanolamine having at least one alkyl radical having from 8 to 14 carbon atoms and having from 14 to 18 total carbon atoms, a lauryl ether of an alkanolamine, lauryl piperidine, lauryl methyl cyclohexylamine, an acylated polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an acylated hydroxyethyl polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an alkyl imidazoline having an alkyl radical having from 7 to 18 carbon atoms, an alkyl guanidine having an alkyl radical having from 7 to 18 carbon atoms, and from 0.02% to 0.05% of a mixed ether having attached to the ether oxygen a poly-

ethylene oxide radical and an aliphatic hydrocarbon radical having from 7 to 18 carbon atoms.

3. An article of manufacture according to claim 1 in which the cellulosic product is in sheet form.

4. The method of improving the spinning step in the production of regenerated cellulose by the viscose process from raw cotton which comprises adding prior to the completion of shredding from 0.01% to 0.2% by weight, based on the bone dry weight of the cotton, of a cation-active amino compound selected from the group consisting of an alkyl amine having from 7 to 18 carbon atoms, an alkyl alkanolamine having at least one alkyl radical having from 8 to 14 carbon atoms and having from 14 to 18 total carbon atoms, a lauryl ether of an alkanolamine, lauryl piperidine, lauryl methyl cyclohexylamine, an acylated polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an acylated hydroxyethyl polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an alkyl imidazoline having an alkyl radical having from 7 to 18 carbon atoms and an alkyl guanidine having an alkyl radical having from 7 to 18 carbon atoms.

5. The method of improving the spinning step in the production of regenerated cellulose by the viscose process from raw cotton which comprises adding prior to the completion of shredding from 0.01% to 0.2% by weight, based on the bone dry weight of the cotton, of a cation-active amino compound selected from the group consisting of an alkyl amine having from 7 to 18 carbon atoms, an alkyl alkanolamine having at least one alkyl radical having from 8 to 14 carbon atoms and having from 14 to 18 total carbon atoms, a lauryl ether of an alkanolamine, lauryl piperidine, lauryl methyl cyclohexylamine, an acylated polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an acylated hydroxyethyl polyethylene polyamine in which the acyl radical has from 7 to 18 carbon atoms, an alkyl imidazoline having an alkyl radical having from 7 to 18 carbon atoms, an alkyl guanidine having an alkyl radical having from 7 to 18 carbon atoms, and from 0.02% to 0.05% of a mixed ether having attached to the ether oxygen a polyethylene oxide radical and an aliphatic hydrocarbon radical having from 7 to 18 carbon atoms.

PAUL HENRY SCHLOSSER.
KENNETH RUSSELL GRAY.

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Certificate of Correction

Patent No. 2,481,692

September 13, 1949

PAUL HENRY SCHLOSSER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 46, for the word "roaming" read *foaming*; same line, for "viscose" read *viscose*; column 7, line 44, for "from" read *form*; column 9, line 63, before "coco-nut" strike out "a"; column 10, line 5, for "monamide" read *monoamide*; column 14, line 4, for "produit" read *product*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of February, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.