This invention relates to the treatment of cellulose films and more particularly to the modification of cellulose fibers by treating a textile or the like by the action thereon of a chemical treating reagent.

One of the principal objects of this invention is the treatment of textiles or the like comprising cellulose fibers whereby the cellulose fibers comprised therein are modified by the swelling and dispersing action of a solution of the cellulose fibers thereby beneficiating the product for many commercial uses and applications. Thus this invention is especially applicable, for example, to the treatment of cotton textiles such as marquettes, voiles, lawns and the like not only to improve their appearance by removing projecting fuzz and by producing increased luster or sheen but also to give a permanently improved hand similar to that produced by starch or other temporary finishes and to confer greater stability against shrinking and stretching during washing and drying.

It is a further object of this invention to provide a method of treating textiles or the like comprising cellulose fibers which can be more readily and economically carried out in commercial production as compared with previously proposed processes intended to obtain one or more of the aforesaid objectives. There are a number of well known processes that have been used or proposed herefore for obtaining at least in part one or more of the aforesaid objectives but whose employment is attended with certain disadvantages and drawbacks as compared with the process of this invention. For example, it has long been known that a strong solution of sulphuric acid will effect a cleansing and stiffening action on cotton fabrics. However, because special equipment has to be employed, the use of strong sulphuric acid and because the process is one which requires extremely close control and which is lacking in flexibility, it has had only very limited use. Solutions of other cellulose parchmenizing agents such as zinc chloride and calcium thiocyanate have also been proposed but have failed to gain acceptance, probably due principally to the cost factors involved.

Another process for the modification of cotton textiles which has been known for very many years and has been used from time to time comprises the application thereto of a superammonium hydroxide solution that is suitably formulated as regards its solubilizing action. However, due to the relatively high proportion and nature of active chemicals used in this process the cost is excessive and in addition the superammonium hydroxide solution is exceedingly unpleasant to work with, especially when conventional textile finishing equipment is used, due to the strong fumes of ammonia. Likewise the use of caustic alcalies containing various metallic alkalesides, such as those of zinc, tin and beryllium, has long been known, although the technical aspects of this type of treatment are still being worked on in an endeavor to effect improvements.

The process of this invention has decided advantages and utility as compared with those previously known or proposed. One of the principal advantages of this invention is the extremely low material requirements for the chemicals which are employed in effecting the desired modification of cellulose fibers, while at the same time the chemicals which are used are moderate in cost and are free of objectionable odor, toxicity or corrosive action. Moreover, the process is one which can be carried out rapidly using conventional textile finishing equipment and likewise is one which can be readily carried out and controlled in obtaining desired production and which is highly effective in obtaining desired modification of textiles composed of or comprising cellulose fibers. The foregoing advantages of this invention will be evident from the following description of this invention including the examples herein described which are illustrative of the practice of this invention.

According to this invention it has been found that cellulose fibers may be successfully modified for the purposes aforesaid by the action thereon in an aqueous medium of a biuret, a copper compound and alkali metal hydroxide. When the biuret and the copper compound are incorporated in the presence of the alkali metal hydroxide, their action on the cellulose fibers is a swelling and dispersing action which, depending on the extent to which it is permitted to proceed, can effect gelatinization or even solution of the cellulose fibers. In addition to copper compounds, nickel compounds may be employed but have been found to be less desirable than the copper compounds. A particular compound of a water-soluble salt of copper or nickel may be employed such as the sulphate, acetate, chloride and nitrate salts. In any case it is the metal of the group consisting of copper or nickel which is significant for the purposes herein stated. It is believed that the action which is used in preparing the reagent, for it is the combination of the biuret with the copper or nickel in the alkaline aqueous medium that affords the reagent that is effective for the purposes herein stated. It is believed that the action which is in the nature of a soluble complex that is formed in the alkaline aqueous medium between the metal and the biuret. Accordingly any compound of a metal selected from the group consisting of copper or nickel compounds may be employed that is reactive with the biuret in the presence of the alkali metal hydroxide in an aqueous medium to form a metal-biuret complex, for example, by way of further example, freshly precipitated copper hydroxide or nickel hydroxide, each of which is substantially water-insoluble, is capable in the presence of alkali metal hydroxide of forming an alkali-soluble complex with the biuret, and may be employed. Moreover, essentially water-insoluble salts of copper and nickel, e. g., cupric phosphate or basic copper sulphate are reacted with alkali metal hydroxide in the presence of the alkali metal hydroxide, and may be employed. However, it is normally preferable to employ a water-soluble salt of copper or nickel. More generally, the metal-biuret complex dissolved in the alkali metal hydroxide solution is referred to herein for the sake of brevity as alkali-biuret-copper or alkali-biuret-nickel, as the case may be, or as alkali-biuret-metal in which the metal is selected from the group consisting of copper and nickel.

As above indicated the concentrations of the aforesaid chemical constituents are relatively high as is necessarily the case because of the relative solubilities of the chemicals as contained in the treating solution. Thus in order to produce a solution of the biuret at the temperatures employed in the process sufficient alkali metal hydroxide must be present to provide at least about 1 molar concentration, i. e., at least about 1 mol of the alkali metal hydroxide per liter. On the other hand when the molar concentration of the alkali metal hydroxide approaches about 6 mols per liter the solubility of the biuret complex with either copper or nickel becomes reduced. Accordingly the solution concentration of the alkali metal hydroxide ranges from about 1 molar to about 6 mols per liter. Such concentration of alkali metal hydroxide may be composed of one or more alkali metal hydroxides. The preferred alkali metal hydroxides are sodium hydroxide and potassium hydroxide. Generally in preferred practice of this invention the con-
centration of the alkali metal hydroxide is of the order of 2 to 3 mols per liter, although very good results are also obtained when the molar concentration of the alkali metal hydroxide is about 4.

The solution concentration of the biuret may vary from about 0.5 to about 80 grams per liter; although it is preferable in the practice of this invention that the solution concentration of the biuret be of the order of 10 to 20 grams per liter. In this connection it may be mentioned that since the molecular weight of biuret is 103, \( \frac{1}{630} \) of the value of biuret concentration in terms of grams per liter gives the approximate molar concentration.

Thus the preferred molar concentration of biuret is approximately 0.1 to 0.2 mol per liter. As regards the metal, i.e. copper or nickel, the proportion of the compound thereof which is used may contain from about 0.5 to 5 of said metal per liter. While ordinarily only a single compound is used in carrying out the process, two or more may be used, for the important consideration is the desired proportion of metal available from any one or more compounds of copper or nickel. The metal compound that is preferably employed is copper sulphate.

The cellulose fibers may be subjected to the treating reagent above described for periods ranging from one or two seconds to several hours and at temperatures ranging from the freezing point of the solution to somewhat above room temperature. The activity of the reagent in most cases is affected by both the temperature and the concentrations of the ingredients in the reagent. While this aspect of the invention will be developed more in detail herein, it may be noted at this point that the activity of the reagent toward cellulose fibers is greater at lower temperatures than at higher temperatures, there being little noticeable effect when the temperature is above that of boiling water, when either or both of the metal and biuret components are reduced to the minima therefor above mentioned the activity of the reagent is lessened. Usually it is preferable that the desired action on the cellulose fibers be accomplished in a relatively short period such as one to three minutes or less in such case rapid and therefore economi cal production may be had in commercial practice of this invention. In this connection it may also be mentioned that if the treating solution is one that is adapted to produce the effect on the cellulose fibers which is desired in a short period such as one to three minutes or less under given conditions, more prolonged treatment under the same conditions may result in excessive gelatinization of the fibers for the purposes intended or even complete destruction thereof. However it may be accomplished by employing other conditions of temperature or other concentrations of ingredients or both the action on the cellulose fibers may be considerably more gradual and the treating period therefore, as forty-eight hours or longer, may be employed. It is thus seen that the process of this invention has the advantage of being quite flexible as regards the conditions under which it may be carried out and of being readily controlled as desired. Moreover, somewhat different effects are obtainable depending on the conditions employed. More generally that treating time is employed which gives the desired effect on the cellulose fibers under the prevailing conditions of temperature and formulation of the treating reagent.

After the cellulose fibers have been modified by treating them with the solution described above the fibers are demineralized by steps including treatment with acid and washing. The acid that is employed may be any acid which is adapted to form with carbon or nickel, as the case may be, a water-soluble salt. Thus any acid, either mineral or organic, may be employed such as sulphuric, hydrochloric, nitric, acetic, formic and oxalic. Ordinarily in typical practice of this invention a 5 to 10% solution of sulphuric acid is used for the purpose and then the fibers are washed so as to remove any unreacted acid as well as the other soluble substances.

In the event of this being a bleached or unbleached cotton fabric, as, for example, a fabric of light-weight and/or open construction such as a marquisette, voile, lawn or the like is contacted with a solution in which the alkali metal hydroxide is the biuret, and a copper compound, preferably a water-soluble copper salt such as copper sulphate, under the conditions aforesaid as regards the ranges of solution concentra tion, temperature and duration of the treating period.

The treating solution may be any aqueous solution that is desired or convenient for contacting the cotton fibers in the fabric with the solution. Thus a fabric may be simply immersed in the solution or suitable equipment may be employed for that purpose. For example, by employing a mercerizing machine or by running the fabric through a padder. However, any other operation or machine may be employed, it being desirable to obtain uniformly impregnated sections of the fabric and preferably to control the amount of solution retained by the fabric. Preferably while subjected to the treating solution the fabric is held under suitably controlled tension by warp and filling, as the result of contacting the fibers with the solution they become strongly swollen, and depending on the severity of the action which takes place, almost gelatinized. As a result the surfaces of the fibers become fused or acquire increased lustre and any projecting fibers or fuzz are effectively removed or compacted to the body of the threads. Moreover, the fibers and threads at their points of contact become adherent to each other to a more or less degree depending on the severity of the treatment.

The action of the treating solution on the cotton fibers can be stopped at any time before the desired effect is obtained by removing the fabric from the solution or by cooling the solution, to stop the reaction. The treating solution may be applied in more than one direction, as maintenance of width is normally regarded as the greater importance, and if desired for pro...
ducing certain effects the setting of the fabric may be accomplished while the fabric is in a substantially tensionless state as required for the employment of tension it is to be understood that the fabric or other material being treated may be in a substantially tensionless state. More specifically as regards employment of tension it is to be understood that the fabric or other material being treated may be in an otherwise substantially tensionless state. After the fabric is set, the fabric is stabilized so that it can be handled freely thereafter. Thus if the fabric is set, the setting may be accomplished by drying the fabric, the subsequent acidification and rinsing steps can be carried out while the fabric is not maintained under substantial tension. However, in the final drying step after acidification and rinsing it is preferable to maintain the fabric under at least appreciable tension so that the fabric will dry in a smoother condition. Only moderate tension is normally desirable during this final drying step because if the tension which is then applied is so severe as to stretch the fabric substantially beyond its dimensions when the fibers became set, such severe stretching has the effect of reducing somewhat the stability of the finished fabric.

While procedures such as those mentioned above have been found to be desirable and advantageous in the handling of the fibrous bodies to be subjected to the alkaline treating solution to modify the cellulose in the manner above described, it has been found that other techniques may be employed having in mind the desirability of removal of the treating chemicals by acid solubilization and washing and the desirability of setting the cellulose fibers and thereby stabilizing the fabric while it is held under tension at the dimensions desired in the finished fabric.

While the process of this invention has been exemplified above in connection with the treatment of cotton fabrics, it is also effective for the treatment of other types of fibrous products or bodies which consist of or comprise cellulose fibers and are such that the treating solution can come into contact with the cellulose fibers. For example, the foregoing description respects the treatment of cotton fibers as an illustrative example. In the treatment of fabrics wherein the fibers are regenerated cellulose fibers. However, regenerated cellulose fibers are somewhat more susceptible to the swelling and dispersing action of the treating solution than cotton fibers and for producing a corresponding effect a somewhat lower concentration of the active reagent, or a somewhat higher temperature, or a somewhat shorter treating period is normally employed as may be desired. With cotton fibers, fabrics composed of regenerated cellulose fibers have been greatly beneficial according to this invention. Fabrics composed or comprising any other cellulose fibers, i.e., flax, hemp, etc., may be subjected to this process of this invention. While this invention is particularly applicable to modifying and beneficiating woven textile fabrics it can also be employed in the treatment of various fibrous webs or sheets consisting of or comprising cellulose fibers, as for example, a web or sheet of unspun cotton, regenerated cellulose or other cellulose fibers. Moreover, the process of this invention is not only applicable to threads, yarns or other strands comprised in a textile fabric, but also is applicable to threads, yarns or other strands as such which are composed of or comprise cellulose fibers. More particularly the process of this invention is of particular benefit in treating a cotton roving which has been partially spun or twisted as compared with an ordinary textile yarn or thread, for as the result of treatment according to this invention the fibers in the partially spun yarn can be caused to become cemented together to any extent desired thereby increasing the strength of the yarn. It can be used without further twisting while at the same time enabling the yarn to be used without sizing. Moreover, by resort to such treatment of a partially twisted yarn according to this invention, pyrolysis is avoided. Such technical novelty of the fiber that goes to waste as the result of combing, usually about 30%, due to the fact that the action of the treating solution in interbonding the fibers in the yarn permits the fibers which are ordinarily removed during combing to be considered as a constituent or part of the improvements that are otherwise sought to be obtained by combing.

While the practice of this invention is particularly adapted to the treatment of fibrous bodies consisting essentially of cellulose fibers, the treating solution is effective to modify cellulose fibers in the manner above described whenever the fibrous body comprises cellulose fibers and especially when the fibrous body comprises cellulose fibers which are intended for use in the manufacture of cellulosic fabrics. More specifically it is to be understood that the cellulose fibers are in interconnecting relation in the body that is treated. Normally, however, the practice of this invention is of particular utility in the treatment of fibrous bodies consisting at least in major proportion of cellulose fibers.

In order for the treating reagent to exercise its modifying effects on the cellulosic fibers with desirable rapidity and effectiveness, the cellulosic fibers should be relatively clean and should not carry an excessive amount of either naturally occurring waxes or other impurities, sizing agents or the like, for if the surfaces of the cellulosic fibers are effectively masked so that the treating solution does not come in contact therewith the modifying action of the treating solution on the fibers will not take place. For example, cotton fibers can be cleansed in any suitable way as by usual boiling off operations with materials such as alkalies, soap, soda ash, silicate solution or the like although even when cotton is in the raw state the cotton fibers may be effectively modified according to this invention. Bleaching is not essential but the cellulose fibers may be previously subjected to any conventional bleaching treatment. If desired, one may apply the treating reagent to a fabric only locally as by applying the treating solution or portions of the fabric which is effective to prevent the treating reagent from contacting the surfaces of the cellulose fibers where the masking material is applied thereto. Alternatively, localized application of the treating reagent may be accomplished in other ways whereby the treating solution is prevented in whole or in part from contacting the cellulosic fibers in predetermined areas of the material being treated.

While in the ordinary case the cellulose fibers can most conveniently be subjected to the treating reagent by dissolving the essential ingredients thereof in a common solution in which the fibers are contained therein other techniques may be employed having in mind the desirability of removal of the treating chemicals by acid solubilization and washing and the desirability of setting the cellulose fibers and thereby stabilizing the fabric while it is held under tension at the dimensions desired in the finished fabric. In the practice of this invention.

It is unnecessary to employ pure biuret in the practice of this invention. The technical biuret has been found useful in the treatment of the cellulosic products of pyrolysis of urea, especially when this pyrolysis is done under conditions such that the yield of biuret is high while that of unreacted urea and by-products is low. In the treatment of the cellulosic materials, especially unreacted urea and by-products of urea pyrolysis, a solution of alkali metal hydroxide is used as a means of setting the cellulose fibers and thereby stabilizing the fabric while it is held under tension at the dimensions desired in the finished fabric. The technical biuret can be produced for use according to this invention at materially lower cost as compared with pure biuret and while it contains a substantial amount of unreacted urea and other reaction products such as cyanuric acid and ammonium. The content of biuret contained in the entire reaction product is determinable by analysis, and sufficient of the reaction product is employed so that the biuret content thereof will provide the desired amount of biuret as the treating reagent. Biuret in admixture with unreacted urea and the by-products of urea pyrolysis is defined herein and in the claims as technical biuret obtained by urea pyrolysis, which material preferably contains at least about 50% of biuret, and is preferably used as the practicing agent of this invention. The technical biuret can be produced for use according to this invention at materially lower cost as compared with pure biuret and while it contains a substantial amount of unreacted urea, which is entirely without effect in the absence of the biuret, likewise has been found to have no detrimental effect when it is present in addition to the biuret during the treatment of the cellulosic fibers.
In preparing a treating solution containing biuret, metal compound and caustic alkali it is preferable to first mix the biuret with either pure or water, and then the metal compound in an aqueous medium and thereafter add the alkali metal hydroxide with stirring, as, for example, by adding a 50% solution of alkali metal hydroxide and finally bringing the solution to desired concentration by dilution with water. While the constituents may be combined by dissolving the biuret in alkali metal hydroxide solution and then adding the metal compound thereupon, mixing has the advantage of converting a portion of the metal to an insoluble oxide. The metal compound should not be added directly to the alkali metal hydroxide if the tendency in each case to convert a portion of the metal to insoluble metal oxide is to be avoided.

The nature of the process of this invention and its objectives and advantages will be more thoroughly understood and consideration of the illustrative examples below set forth:

**Example 1.** A piece of plain marquisette, 48 x 28, made of 40% cotton warp and 50% cotton filling was boiled off an hour, then stretched on a pin frame approximately 18 inches square and was immersed for one-half minute at ordinary room temperature of approximately 25°C in a solution containing 12 grams per liter of biuret, .03 mole per liter of CuSO₄, and 3 moles NaOH per liter, and then rinsed, blown free of excess moisture and placed in an oven to dry. The sample was thereafter removed from the pin frame, acidified in 4% H₂SO₄, washed, and replaced on the pin frame for drying. This sample had an excellent appearance due to the removal of fuzz but had a rather limp hand whereupon the experiment was repeated, the same in all particulars except that the immersion time was increased to one minute. The second sample had equally as good an appearance and a much better hand.

**Example 2.** A solution was made up containing 12 grams per liter of pure biuret, and .03 mol per liter of copper as CuSO₄ in 3.5 molar caustic (NaOH). A sample of bleached marquisette as used in Example 1 was supported on a pin frame approximately 18 inches square and immersed in this solution for three minutes at room temperature, rinsed, and blown dry, followed by acidification and redrying as in Example 1. 38 grams per liter of pure urea were then added to the solution and a second sample was run under the same conditions as the first. Both samples were excellent in appearance and hand, there being no noticeable difference due to the presence or absence of the relatively large amount of urea that was present.

**Example 3.** A further sample of the same marquisette, boiled off and bleached in the conventional manner as treated to have a piece of the fabric approximately two yards long by one-half yard wide was weighed, dry, and saturated for one minute at 25°C in a solution containing technical biuret obtained by urea pyrolysis (comprising about 60% of the pure and about 38% of nonreacted urea together with the other reaction by-products) in sufficient amount to give 10 grams per liter of biuret, and .025 mole per liter of copper as copper sulphate in 3 molar NaOH. Strong swelling of the threads took place accompanied by a marked shrinkage of the fabric which was very slight. At the end of one minute, the fabric was passed through squeeze rolls and was weighed again to determine the pick-up, which was found to be approximately 320%. The material was then framed to its original dimensions, rinsed slightly in cold water, blown off with compressed air to break the film of the adhering liquid, and dried at 65° to 70°C, after which it was removed from the frame, acidified in 6 to 8% sulphuric acid, washed thoroughly and dried again on the frame at its original dimensions. This sample then had an excellent crisp hand and the interstices were quite clean and free of the usual fuzziness. After a wash test performed by the standard ASTM procedure D-437-36 for cotton fabrics, the shrinkage was as follows:

<table>
<thead>
<tr>
<th>Warp, percent</th>
<th>Filling, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1, 3.8, 3.6; av. 3.5</td>
<td>3.1, 4.1; av. 3.6</td>
</tr>
</tbody>
</table>

**Example 4.** A sample approximately two yards long by one-half yard wide of the same material as used in Example 1, having been given the same pretreatment, was then treated in the alkaline copper-biuret solution in the following manner:

The material was saturated in the loose state in a solution containing technical biuret, obtained by urea pyrolysis equivalent to 5 grams per liter of biuret and .0125 mol per liter of copper as CuSO₄ in 3 molar NaOH at a temperature of approximately -5°C. After saturating for one minute, the materials were passed through squeeze rolls and through a double dip in cold water, the time of exposure being approximately two seconds, followed by a second passage through squeeze rolls after which the sample was framed to the original dimensions and dried. The material was then acidified, washed and dried as in Example 3. It had an excellent hand and clean appearance, and showed a shrinkage after the standard ASTM test D-437-36 of approximately 4% in the warp and 5% in the filling. As a check, one portion of this material was acidified in the wet state immediately after it had been framed to the original dimension but this sample was found to have less appearance and greater shrinkage than the samples which had been dried previous to the acidification.

**Example 5.** A sample of the same material as used in Example 1, two yards long x 1½ yards wide was padded (through 2 dips and 2 nips) with the same solution as used in Example 3, and at the same temperature. The total time from the first dip to the last nip was about seven seconds. The fabric was then framed to its original dimensions, blown off with compressed air, and oven dried at approximately 65° to 70°C. The material was then removed from the frame, acidified in 6% H₂SO₄, washed free of acid, reframed to its original dimensions and dried again. The finished material had a good clarity and the moderately crisp hand of a light starch. After a wash test by the ASTM method D-437-36 warp and filling shrinkages were found to be 3.1% and 4.3%, respectively.

**Example 6.** A piece of plain marquisette approximately the same size and from the same source as used in Example 4 was given the same sequence of treatments as described in that example with the exception of the temperature, which was not raised to above 5°C. The solution was reduced to 2.5 grams per liter and .00625 mol per liter respectively, the NaOH concentration remaining unchanged at 3 mols per liter, and that the temperature of the solution was maintained at -5°C. The treated fabric, after completion of the after treatments as detailed in Example 4 including drying prior to acidification exhibited a similar removal of interstitial fuzz as in that example, but to a somewhat lesser degree. About the same enhancement in the stiffness or hand was produced, however. The experiment was then repeated with the same solution but at -5°C. and the time of treatment was increased to five minutes. The results in this case were substantially the equivalent of those previously obtained at the lower temperature although no means of quantitative estimation were available.

**Example 7.** A fabric of the same construction as used in Example 1 having been given the same pretreatment, was stretched on an 18 inch square pin frame and immersed for three minutes in a solution containing 10 grams (approximately .1 mol) per liter of biuret, .05 mol per liter of copper as CuSO₄, and 2.0 mols per liter of NaOH, the solution being acidified in temperature or approximately 23°C. The fabric was rinsed lightly with cold water and dried on the frame in a current of warm air, following which the fabric was removed, acidified in 6% H₂SO₄, washed, reframed, and dried. This finished fabric was completely free of fuzz and had a desirable hand of moderate stiffness as compared with the absolutely limp hand of the untreated fabric.
Example 8.—A series of solutions was made according to the following table:

<table>
<thead>
<tr>
<th>Biuret</th>
<th>Grams per Liter</th>
<th>Mols per Liter (Approximate)</th>
<th>CuSO₄ Mols per Liter</th>
<th>NaOH Mols per Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.125</td>
<td>0.025</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>1.88</td>
<td>0.182</td>
<td>0.036</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2.56</td>
<td>0.242</td>
<td>0.052</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3.25</td>
<td>0.292</td>
<td>0.064</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3.75</td>
<td>0.352</td>
<td>0.076</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4.38</td>
<td>0.438</td>
<td>0.088</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6.00</td>
<td>0.600</td>
<td>0.120</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6.25</td>
<td>0.625</td>
<td>0.125</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

It will be noted that in this experiment the molar ratio of biuret to copper is approximately 5 to 1 in each solution. Samples of marquiseette approximately 3 inches square having been previously treated as in the preceding examples were supported on a glass frame and given a three minute immersion in each of the solutions shown. All samples while supported in the frame were rinsed, blown dry, acidified in approximately 6% sulphuric acid, washed and redried, and the results compared. All samples with the exception of the first were well cleared of fuzz and showed an increasing stiffness with increasing biuret and copper concentration, the last showing complete fusion of the thread surfaces and a pronounced stiffness on the back of hand. Example 9.—Three solutions were made up according to the following table:

<table>
<thead>
<tr>
<th>Biuret</th>
<th>Grams per Liter</th>
<th>Mols per Liter (Approximate)</th>
<th>Cu (as CuSO₄) Mols per Liter</th>
<th>NaOH Mols per Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Samples of plain cotton marquiseette approximately 3 inches square, pretreated as described in previous examples, were supported on glass frames as described in Example 8, and treated with the respective solutions at 70°C. It was noted that the background of the fabric had undergone a clearing and stiffening as obtained on plain marquiseette by immersion in similar treating solutions while, at the same time, the decorative spots or ruffs retained their stiffness to a large degree. Example 12.—A piece of voile, 60 x 52, made of 50% cotton warp and 60% cotton filling was boiled off and bleached and then treated on a pin frame in the usual manner. It was then immersed in the usual manner.

It will be noted that the spots was a paraffin wax composition containing an oil soluble water dispersible emulsifying agent whereby the removal of the protecting agent after the treatment of the emulsifying agent to be employed in any such operation is a relative lack of activity at the temperature at which the treating solution is maintained when it is contacted with the fabric. A suitable emulsifying agent which is relatively inactive at room temperature or below is available under the trade name of “Avonol-WD.” Example 11.—A sample of clip spot marquiseette as used in Example 10 approximately 10 inches long was drawn lightly across a rubber roll which was rotating in a solution maintained at 0°C and containing 12 grams per liter of biuret, 0.03 molar per liter of copper as CuSO₄, and 3.5 mols per liter of NaOH, the back or reverse side of the fabric being presented to the roll which was lightly wetted with the treating solution. Following this “back-filling” operation, the sample of fabric was placed on a pin frame, approximately 18 inches long and square, and immersed for three minutes in the same solution as used in Example 10 at the same temperature. At the end of the three minute interval, the sample was rinsed lightly, blown free of excess moisture and film, and dried in the oven at 65° to 70°C. After drying the sample was removed from the frame, acidified in 6% H₂SO₄, washed free of acid, and replaced on the frame for drying. This treatment produced a beautifully sheer appearance, the component yarns being partially defuzed and fused. Example 13.—A piece of bleached lawn, 76 x 72, was supported on a pin frame and immersed for approximately 4½ minutes in a solution containing 24 grams per liter biuret and 0.06 molar per liter of copper as CuSO₄ in 4.0 molar NaOH at a temperature of 18°C. After draining for ½ minute, the sample was then transferred to a second solution containing ½ as much biuret and copper and ½ as much NaOH as the first and left to stand for 2 minutes in order to soak for approximately 5 minutes in order to dissolve any interstitial material gelatinized but not dissolved by the first solution. With no further rinsing, the sample then dried at 65° to 70°C for 20 minutes after which it was acidified, washed, and dried in the usual manner. The finished fabric had the excellent clarity and crisp hand of a conventional organdy.

Example 14.—The treatment as described in Example 10 was extended to samples of broadcloth and Oxford cloth with very similar results: In the case of the broadcloth, the fabric gained a moderately stiff hand and a pleasing sheen coupled with a loss of opacity, however, which would bar it from the usual applications of broadcloth. In the case of the Oxford, the diminution of the thread (filling) diameter was so great that the fabric entirely lost its original character, and became a stiffened open mesh material such as is used for interlining in suit construction.

Example 15.—A length of 12's carded cotton yarn of 10.4 turns per inch in the raw state with the naturally occurring waxes and other impurities remaining on the fibers was supported on an open frame so as to maintain its original length but with a view to the avoidance of contact between adjacent yarns, and the yarn was then immersed without further treatment for three minutes in a solution containing at 10°C. containing approximately 24 grams per liter of biuret, 0.03 molar per liter of copper as CuSO₄ and 4 mols per liter of NaOH. Thereafter it was immersed directly in a solution containing approximately 5% of H₂SO₄, and then was thoroughly rinsed and dried. The yarn was reduced in diameter, and had a smoother appearance and was somewhat stiffened with a breaking strength was increased from 97 pounds for the untreated yarns to 1.68 pounds for the treated, while the respective elongation at the break was reduced from 6.6% in 10 inches to 4.5% for the respective samples.
Example 16.—Solutions of the following compositions were made up and tested for their power of dissolving or fusing the fuzzi on ordinary untreated cotton yarn (12's) of the type mentioned in Example 15 with the following results for a test period at which comparative results were observable:

<table>
<thead>
<tr>
<th>Biuret</th>
<th>Cu as CuSO4</th>
<th>KOH</th>
<th>Effect In Three Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams per Liter</td>
<td>Mols per Liter</td>
<td>Mols per Liter</td>
<td>Mols per Liter</td>
</tr>
<tr>
<td>(g)</td>
<td>60</td>
<td>0.78</td>
<td>0.30</td>
</tr>
<tr>
<td>40</td>
<td>0.40</td>
<td>0.20</td>
<td>4.2</td>
</tr>
<tr>
<td>20</td>
<td>0.20</td>
<td>0.10</td>
<td>2.1</td>
</tr>
</tbody>
</table>

All solutions dissolved the yarn completely in longer time.

Example 17.—An experiment was performed under exactly the same conditions as in Example 7 except that the solution was made 2 molar in KOH instead of NaOH. The results on this fabric were entirely comparable with those previously obtained with NaOH, the binding perhaps slightly thinner, or more for paper.

Example 18.—A solution was made containing 24 grams per liter of biuret, .06 mol of copper as cupric acetate, and 16 grams per liter of NaOH. This solution was then tested with 12's cotton roving as in Example 16 and found to be quite effective. There was no apparent gain in solvent activity of this solution for cotton over those prepared from CuSO4, although it was noted that the preparation of the solution was undoubtedly facilitated by the substitution of the acetate for the carbonate salt. Solutions were also made containing 10 grams per liter of biuret, 3.6 mols per liter of NaOH, and .05 mol per liter of copper as the acetate, chloride and nitrate respectively. All solutions were tested under comparable conditions upon small pieces of cotton marquisette and found to be substantially the equivalent of similar solutions made by using CuSO4 as the source of the soluble copper in having marked powers of removing the interstitial fuzz and fusing the yarn surfaces to confer an increased luster and stiffened hand upon the fabrics so treated.

Example 19.—A solution was made containing 10 grams per liter of biuret, .05 mol per liter of nickel as NiSO4 and 2.0 mols per liter of NaOH. This solution was a deep orange yellow and was found to possess a moderate solvent activity toward cellulose, especially at -20°C. The nickel, much inferior to that exhibited by the corresponding copper-containing solutions, in equivalent molar strengths.

Example 20.—A piece of boiled off but unleached plain cotton marquisette of 40's warp and 50's filling was impregnated with a slurry of a biuret-copper complex made by adding a calculated amount of CuSO4 solution to a slurry of technical biuret obtained by urea pyrolysis containing a known quantity of biuret, approximately 0.6 mol per liter, the stoichiometric ratio being 1 mol copper to 2 mol biuret. No apparent reaction took place. After partial drying the fabric was immersed in 3 molar NaOH for one minute at approximately 25°C while being supported on a frame. The characteristic purpel of the alkaline copper-biuret complex appeared at the surface of the cloth and shrinking was observed. After the caustic treatment the excess solution was blown off with a compressed air jet and the fabric was acidified, washed with water and dried completely and dried while still on the frame. Considerable clearing or removal of the interstitial fuzz was obtained by this sequence of treatment and the fabric was stiffened as in the treatment with the alkaline copper-biuret complex was used in homogeneous solution. The above experiment was repeated with the modification that the copper-biuret complex was dried onto the fabric at approximately 70°C after removing the excess by paper rolls and the strength of the NaOH was increased to 5 mols per liter. In the latter treatment the fabric was slightly less stiff and less chalky in appearance.

Example 21.—A piece of rayon fabric 3.8 yards/pound having a viscose filament warp and spun viscose filling, commonly known as fuji cloth was boiled off for one hour in 2% soda ash, and after rinsing and drying was treated, while supported under moderate tension on a suitable frame, with a solution containing 1 mol per liter of NaOH, 1.0 molar liter of copper as cupric sulfate and 2.06 grams or .02 mol per liter of biuret for approximately 60 seconds at room temperature of 27 to 28°C. After this treatment the excess solution was shaken off and the fabric still supported on the frame was dried at approximately 50 to 60°C, and was then neutralized in approximately 6 to 8% H2SO4, rinsed thoroughly in warm water, and acidified as previously done. This fabric had a much more desirable hand than the untreated material, being firmer and fuller.

The experiment was repeated with another piece of the same fabric and with the same solution as before, except that the temperature of treatment was reduced to 9 to 10°C and the time to 30 seconds, all other steps of the treatment being substantially the same. In this case the finished fabric had a very pleasing hand quite similar to that given by a light starching.

That these improvements were not due to the known action of dilute caustic on regenerated cellulose was checked by subjecting another piece of the same fabric to the action of 1 mol per liter NaOH alone for 30 seconds at room temperature and following the same schedule of after treatments. In this case the fabric acquired a quite undesirable hand for 30 seconds, comparable to the enhanced effect previously noted.

Example 22.—A small piece of the fuji cloth as used in Example 21 was supported on a glass frame and was subjected to the action of a solution containing 2 mols per liter of LiOH, .05 mol per liter of copper added as copper sulphate and 10 grams or approximately .1 mol per liter of biuret for a period of about 30 seconds at 8 to 9°C. After which the treated sample was acidified directly in approximately 6 to 8% H2SO4 and rinsed and dried. The resulting fabric was markedly stiffened, without, however, exhibiting a glazed or parchmented finish.

Example 23.—A piece of linen fabric, 76 x 76, as commonly used for handkerchiefs was immersed in solution containing 4.0 mols per liter of NaOH, 1.0 molar liter of copper as cupric sulfate, 0.2 mol per liter of CuSO4 and .05 mol per liter of biuret (the latter being substantially pure) for a period of 30 seconds at a temperature of approximately 17°C, was then rinsed in cold water and dried at approximately 60°C, after which it was acidified in 6 to 8% H2SO4 and was then thoroughly rinsed and reddied by ironing flat, the fabric being maintained in a substantially tensionless condition throughout this sequence of treatment. The fabric was brightened and gained an excellent hand similar to a light starch, and at the same time showed no undesirable thinning.

As is apparent from the foregoing examples the solution concentration of the chemical ingredients of the treating reagent is low, and this is particularly the case as regards the concentration of the copper and/or nickel comprised therein. This is in accordance with the general practice of the process of this invention involves using an amount of copper, for example, which is only 1/10 or even less of the amount of copper which is used in the cuprammonium hydroxide type of treatment or the amount of metal as metal oxide which is used in the type of treatment wherein caustic alkali is activated by metal oxides such as those of zinc, tin and beryllium.

While the foregoing as regards the solution concentration of the chemical ingredients of the treating reagent used according to this invention is of general applicability, it is to be understood that the particular concentration that is employed in any case will depend upon such factors as the rate of action on the cellulose fibers that may be desired, the temperature at which the treatment is performed, and the effect on solubilities of such factors as temperature, the molar concentration of the alkalai metal hydroxide and the molar ratio of the biuret to the metal. Generally speaking as the temperature is lowered the solubility of the biuret and metal-biuret complex is decreased, but while decrease in temperature may be offset by the increase in activity or solvent power toward cellulose which results from using the lower temperature.
Thus, for a given solution the maximum rate of action on the cotton fibers is afforded at a temperature in the neighborhood of 50° C. with gradual decrease in activity up to a temperature of about 55° C., at which the rate of action is very slow. As hereinafore stated lower temperatures such as 10° or 12° C. may be employed down to the freezing point of the solution. For the expedient treatment of fabrics with minimum solution concentrations, temperatures of the order of 5° C. to 10° C. are preferred although the process may be carried out in an ordinary room temperature, namely, about 20° C. to 25° C. Maximum solubility of the metal-biuret content is obtained when the molar ratio of biuret to metal is of the order of about 2:1 and when the molar concentration of the alkali metal hydroxide is in the neighborhood of 5 C, with substantial tension, while the fabric is maintained under substantial tension, neutralizing and demineralizing said fabric by contacting the fabric with a dilute acid which forms with copper a water soluble salt and rinsing the fabric, and drying the fabric under at least appreciable tension.

2. The method of claim 1 wherein the molar ratio of the biuret to copper ranges from about 2:1 to about 5:1 and the molar concentration of the alkali metal hydroxide ranges from about 2 to about 4 mols per liter of said alkali metal hydroxide, the molar ratio of said biuret salt ranging from about 2:1 to about 4:1.

3. A method of treating a cotton fabric which comprises the steps of contacting the cotton fibers comprised in said fabric with an aqueous solution having dissolved therein from about 1 to about 6 mols per liter of alkali metal hydroxide selected from the group consisting of sodium hydroxide and potassium hydroxide until said cotton fibers have been substantially swollen and gelatinized, thereafter and prior to substantial disintegration of said cotton fibers drying the fabric while maintained under substantial tension, neutralizing and demineralizing said fabric by contacting the fabric with a dilute acid which forms with copper a water soluble salt and rinsing the fabric, and drying the fabric under at least appreciable tension.

4. The method of claim 3 wherein said solution has dissolved therein from about 1 to about 20 grams per liter of biuret, about .03 to .1 mol per liter of said copper, and about 2 to about 4 mols per liter of said alkali metal hydroxide, the molar ratio of said biuret salt ranging from about 2:1 to about 4:1.

5. A method of treating a cotton yarn which comprises contacting cotton fibers comprised in said yarn with an aqueous solution having dissolved therein from about 0.5 to about 80 grams per liter of biuret, ionizable copper containing compound containing from about .0025 to about .25 mol per liter of copper from about 1 to about 6 mols per liter of alkali metal hydroxide selected from the group consisting of sodium hydroxide and potassium hydroxide until said cotton fibers have been substantially swollen and gelatinized, and thereafter and prior to substantial disintegration of said cotton fibers neutralizing and demineralizing said yarn by contacting the yarn with a dilute acid which forms with copper a soluble salt and rinsing, and drying the yarn.

6. A method of treating cellulose fibers to modify said fibers which comprises contacting said fibers at a temperature below about 50° C. with an aqueous solution of alkali metal hydroxide containing dissolved therein a complex product of reaction between biuret and ionizable compound of metal selected from the group consisting of copper and nickel, the concentrations of said alkali metal hydroxide, said biuret and said metal in said solution contacted with said fibers being between about 1 and about 6 mols per liter, respectively, and neutralizing said fibers in contact with said solution until said cellulose fibers are substantially swollen and gelatinized.

7. The method of claim 6 wherein said cellulose fibers are removed from said solution from contact therewith and neutralizing and demineralizing said fibers by contacting said fibers with an acid and removing the fibers to remove soluble substances therefrom.

8. The method of claim 6 wherein said biuret is biuret comprised in technical biuret obtained by pyrolysis of urea.

9. The method of claim 6 wherein the molar ratio of said biuret to said metal ranges from about 2:1 to about 5:1.

10. The method of claim 6 wherein said cellulose fibers are comprised in a fabric consisting predominantly of fibers selected from the group consisting of cotton fibers and regenerated cellulose fibers and wherein said removal of said solution from said cellulose fibers comprises drying said fabric while said fabric is maintained under substantial tension followed by neutralizing and demineralizing said cellulose fibers.

11. The method of claim 6 wherein said cellulose fibers are comprised in a fabric consisting predominantly of fibers selected from the group consisting of cotton fibers and regenerated cellulose fibers and wherein said removal of said solution from said cellulose fibers comprises drying said fabric and plying dilute acid to said fabric for neutralizing said alkali metal hydroxide while said fabric is maintained under substantial tension, said fabric thereafter being rinsed to remove soluble substances therefrom.
12. A method of treating cellulose fibers comprised in a textile fibrous body which comprises the steps of contacting said fibrous body with an aqueous alkaline solution comprising from about 1 to about 6 mols per liter of alkali metal hydroxide, said hydroxide being selected from the group consisting of sodium and potassium hydroxide, and a metal-biuret complex formed in said alkaline solution by the reaction between biuret and metal contained in an ionizable metal compound, said metal being selected from the group consisting of copper and nickel and being present in said solution in the range of from about .0025 to about .25 mols per liter, said biuret being present in the range from about .05 to about .75 mols per liter, the molar ratio between said biuret and said metal being maintained between about 2:1 and about 5:1 over the range specified, said contact between said fibrous body and said solution being maintained until said cellulose fibers have been substantially swollen and gelatinized, and thereafter separating said fibrous body from the said solution and neutralizing and demineralizing said fibrous body by contacting it with a dilute aqueous acid solution which forms a soluble salt of said metal used in conjunction with said biuret and thereafter rinsing said fibrous body free of acid and drying same.

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