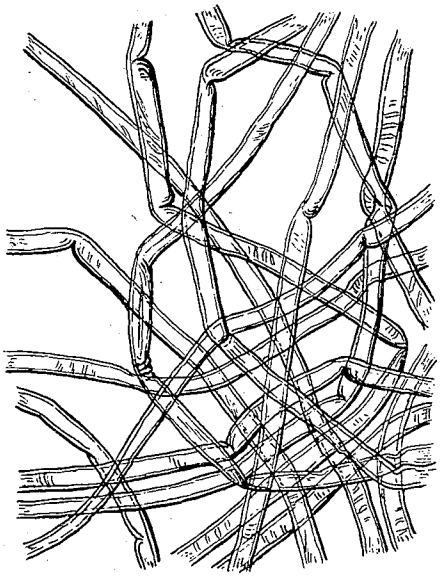
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FIBROUS FELTING OR FELTED PAPER PRODUCT AND PROCESS OF MAKING SAME

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FIBROUS FELTING OR FELTED PAPER PRODUCT AND PROCESS OF MAKING SAME

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The invention relates to the production, from commercial cellulosic fibrous material, of a felted product in which the qualities of absorbency, capillarity, bulkiness and pliability may be relatively controlled by the use of caustic soda solution of varying strengths, but of less than mercerizing strength, in connection with certain cellulose reactive compounds such as copper, zinc or aluminum compounds, and in connection with a substance to hold in solution the hydroxides of copper, zinc or aluminum. These qualities may be controlled by the variation of the concentration of caustic soda solution which, if desired, may be held constant for a given treatment and the relative proportion of copper, zinc or aluminum compound present in the mix, based on the weight of the fibre.

By basing the relative proportion of the copper, zinc or aluminum salt on the weight of the fibre and not on concentration of solution I find that in the production of my material, it will not be necessary to stop off the reaction by dilution, heating, neutralization or by any other means inasmuch as the actuating copper, zinc or aluminum chemical will have been used up or withdrawn from solution by the fibre.

The invention also relates to kinking of fibres with caustic soda solution of non-mercerizing strength in combination with a physico-chemical activator or accelerator of non-mercerizing activity without materially changing the cross-sectional, ribbon-like shape of the fibres, but causing a series of retroversions or inclines and anticlines or hinged convolutions along the fibre length.

The invention also relates to the kinking of fibres by a solution which does not decrease the yield of finished product or increase the shrinkage as much as does caustic soda solution of mercerizing activity.

The invention also relates to the production of an abrasion resisting felting pulp which may be mechanically treated in the felting operation by the ordinary paper mill equipment without the formation of a prohibitive amount of comminuted material which may prevent the formation of a satisfactory felted sheet.

The invention also relates to a method of preserving the curling of the fibres and at the same time coloring the fibres or imparting color to fibres without changing the curled or non-curled condition of the fibres.

The invention also relates to the provision of a fibrous product, the fibres of which are fixed or set as to shape by a chemical or physico-chemical encasement or coating deposit.

The invention also relates to the treatment of metallic compound encased fibrous product with a substance to supplant the metal compound of the encasement by another metal compound.

The invention further relates to treatment of the encased fibrous product with a substance to provide a mucilaginous binder.

Further, the invention relates to the removal of the fibre encasement only after formation into felt.

The invention further relates to the controlling of the activity of caustic soda solutions of mercerizing strength, when using the method of curling of fibres set forth in my Patent No. 1,830,131. This control may be effected by the heating of the fibrous mass or by the decrease of the amount of activating agent such as copper, zinc or aluminum compounds to cause a slowing of the fibres, or by the increase of the amount of copper, zinc or aluminum compounds with the decrease of the heating to make the fibres freer or less obstructive to water passage. If it is desired to produce the encased fibres without the kinked or curled characteristics, this may be done to any desired degree by temperature elevation during the chemical treatment.

An object of the invention is the production, from commercial cellulosic fibrous material of a felted product in which the qualities of absorbency, capillarity, bulkiness and pliability may be relatively controlled by controlling the proportions of chemicals used to effect certain definite characteristics of fibre outline.

Another object is the employment in producing a felting pulp, of caustic soda solution of less than mercerizing activity so that the fibre wall may not be swollen or rounded to any appreciable extent and the employment of another chemical or chemicals such as copper, zinc, or aluminum salts or compounds, together with a substance which will hold the hydroxides of the metals of these salts in solution so that these hydroxides in solution working with the caustic soda or caustic lye may cause the fibres to twist and turn but do not cause the fibre cross-section to lose its general ribbon-like characteristic.

Another object is to avoid the necessity of stopping off the reaction by dilution, heating, neutralization, or other means, by basing the relative proportion of the copper, zinc or aluminum compound on the weight of the fibre and not on concentration of solution, whereby the activating copper or zinc chemical will be used up or withdrawn from solution by the fibre.

Another object is to produce fibres having im-

proved water suspension felt forming characteristics which are gained by reacting with cellulose fibres and depositing thereon physico-chemically a substance having greater specific gravity than the cellulose fibre itself.

Another object is to produce a resilient felting pulp with minimum shrinkage of raw material.

Another object is to produce a resilient felting pulp which may be mechanically worked by the ordinary refining equipment of a paper mill such as a Jordan engine without the formation of an undue amount of fines.

Another object is to provide a method whereby one or more of the treating agents or treating agent products is permitted to remain on the fibres to provide an encasing and preserving effect or may be chemically changed to provide a coloring effect without uncurling the fibres or without altering their curled or non-curled condition.

Another object is to provide a fibrous product the configurations of the fibres of which are set in varying degrees of shape by a chemical compound encasement or physico-chemical coating or deposit. This set may be in respect either to straight fibres or curled fibres or a mixture of the two, depending upon the degree of absorbency, bulkiness, capillarity, and pliability which may be desired.

Another object is to provide a treatment supplanting the metal compound of the encasement on the fibre by another metal compound.

A further object is to provide a mucilaginous binding of the product by treatment of the encasement with a suitable material.

Another object is the removal of the fibre encasing substance from the felted product only after fibre interlocking has taken place in order not to disturb the correlative position of the fibres nor to substantially change the voids in the finished felt.

Another object relates to the controlling of the activity of caustic soda solutions of mercerizing strength when using the method of curling of fibres set forth in my Patent No. 1,830,131. This control may be accomplished by the heating of the fibrous mass or by the decrease of the amount of activating agent such as copper, zinc or aluminum salts to cause a slowing of the fibres, or by the increase of the amount of copper, zinc, or aluminum salts with the decrease of the heating to make the fibres freer or less obstructive to water passage.

Other objects will appear from the following disclosure:—

The drawing shows the flat ribbon-like encased fibres resulting from my process.

I have found that in the commercial outlets for absorbent felt, certain types of finished product such as dielectric paneling may require a hard, stiff, absorbent felt while another type of finished product, such as artificial leather, may require a pliable felt. Again, one type of finished material may necessitate a high capillarity toward such a solvent as benzol, or another may require a high capillarity toward water. Heretofore the production of absorbent felts of different fibre characteristics has been accomplished by a difference in concentration and temperatures of caustic soda solution of mercerizing strength but does not permit of marked relative control of the various fibre characteristics. My present method involving holding the strength of the caustic soda used in the treatment to below mercerizing activity provides improved and distinct relative control of the various fibre characteristics. I am able to retain the ribbon-like cross-sectional shape of the fibres and control the voids in the felted sheet by the use of a copper solution in connection with caustic soda solution of less than mercerizing activity. I am able by varying the concentration of caustic soda treating solution, which may be kept constant for a given treatment, and by varying the ratio of the weights of copper or zinc salts to fibre weight, to change the physical characteristics of the fibres from a very slight distortion to a curling such that the fibres are almost rolled into balls. It is, of course, necessary to have a certain amount of fibre length in order for the fibres to have felting properties.

It is apparent that the absorbing power of any sheet is a function of the capillary characteristics or shapes and sizes of the interstices between adjacent fibres. Sand has capillarity yet sand has no fibrous nature. A mass of fibre rolled or curled into balls has capillarity yet a fibrous mass constituted of such balls of curled fibre has very little felting power or tensile strength which is ordinarily expected and required of sheeted fibres. I have determined that capillarity and the speed at which water will drain through a mass of felted fibres, commonly designated "freeness" are not necessarily corresponding functions of the fibre mass. The reason for this is that flat fibres when placed side by side will hold more liquid between their flat surfaces by capillary force than will be held between the surfaces of two similarly placed fibres of rounded cross-section and of the same displacement. In other words, flat, untreated, finished or prepared fibres may have greater capillarity but with less freeness than finished or prepared fibres treated until they become rounded, which latter may have relatively low capillarity with high freeness.

If it is desired to absorb any particular fluid by capillary attraction throughout a felted fibrous sheet or mass, it is first necessary to rid the fibres of any substance or substances which may naturally repel the fluid to be absorbed. The second step which is necessary is to so change the physical shape of the fibres that, after having been rid of any fluid repelling substance or substances, the fibres may lie in relative positions which will produce optimum results in the desired physical properties of the finished product.

In controlling the qualities of my product I use a comparatively weak solution of detergent such as caustic soda, of less than mercerizing strength, which in itself, has, at mercerizing strengths, a marked effect upon the physical shape of cellulose fibres.

The difficulties in controlling the amount of physical change of the fibres, when using a strong caustic soda solution to effect this change, are due to the counter or curl inhibiting effects of mechanical agitation and temperature changes. I have sought and have discovered a method whereby the physical characteristics of the individual fibres, and consequently the physical characteristics of the felted sheet of fibres may be controlled not alone by concentration of treating solution, changes in temperatures, or by diluting by water at a certain point, but by adding an amount of another type of material to the fibre and deterging solution, based not upon concentration of solution but upon the weight of the fibre in the mixture. Flowage and hydraulics does not enter into this control method, nor does an excessive amount of treating chemical have to be added, nor is an uncertain stop-

ping off of the action at a predetermined point necessary. The dry weight of the cellulose fibre would of course be known. The deterging caustic soda solution may be held constant as to concentration in a given treatment. The physical transfiguration or change in form of the fibres may be effected by adding a certain proportional weight of chemical based on the weight of the fibre in the mass being treated. Due to the exhaustion and complete absorption by the cellulose of all of the accelerating or activating chemical no stopping off by dilution, acid neutralization or other means is required. Of course, it will be seen that a higher concentration of primary or deterging chemical, i. e., caustic soda, might be used and a lower ratio of secondary chemical, i. e., copper, zinc or aluminum salt with proper hydrate anti-precipitant, based on the weight of the pulp, might be used and still obtain a certain freeness result but with a difference in pliability or bulkiness or capillarity or absorbency. These possible variations in the process make my method more flexible as to the various characteristics which I am able to obtain in my finished product.

According to methods heretofore proposed, when using strong caustic soda solutions, or other mercerizing agents, whose curling reactivity may be of mercerizing effect, i. e., based on concentration of treating solution rather than on a certain relation of weight of reactive chemical to weight of pulp, it will be evident that it is necessary to use an excess of treating solution as a vehicle or wetting agent for the pulp. In the case of the use of caustic soda of mercerizing strengths, it often happens that less than 2% of the weight of caustic soda present is actually consumed or changed over chemically as the result of chemical or physico-chemical reaction. Therefore, it will be seen that if 98% of the caustic soda present is left to continue its work there must be some stopping off of the reaction by chemical or physico-chemical means such as dilution, acid neutralization, heating, squeezing or a combination of these things so that the desired product may be obtained. In actual practice, this stopping off is extremely difficult to control as a freeness test requires the taking of a sample, bringing the sample to a constant moisture test, weighing and going through the manipulations of any of the well known freeness tests before a change in control may be intelligently undertaken. My method does not require any stopping off. The extent of my physico-chemical reaction is predetermined by the weight of copper, zinc or aluminum salt which I add to a certain weight of pulp, simply using a vehicle of weak caustic of less than mercerizing strength which can do no harm after the activating chemical is withdrawn from the solution.

I have tested and have manufactured my product from over thirty varieties and brands of cellulose fibre. The grades of fibre used include rag and linen fibres, cotton linters, bleached and unbleached sulfite wood pulps, bleached and unbleached soda wood pulps, bleached and unbleached sulfate wood pulps, paper chippings and scrap paper. I have found the freeness of these commercial fibres to vary from 325 c. c. for cotton linters treated with 1% caustic with very little chemical treatment up to a jelly like mass through which the water could scarcely drain. These illustrations are, of course, extremes and the practical part of my work has been confined mainly to three well known general classes of wood fibre, namely, unbleached sulphite, bleached sulphite and kraft or unbleached sulphate.

Below are illustrative figures showing variation in freeness in commercial fibres, also the effect on freeness of treating with 6% caustic soda, with 18% caustic soda and with 6% of caustic soda and then with an amount of copper salt equivalent to 8% by weight of copper oxide based on the weight of the fibre.

	Original freeness c. c.	Freeness 6% NaOH solution treatment c. c.	Freeness 18% NaOH treatment c. c.	Freeness 6% NaOH solution 8% CuO added on basis of fibre weight c. c.
Unbleached sulphite	610 670	560 555	420 410	425 423
Bleached sulphite	440 583	430 552	380 405	385 414
Kraft or unbleached sulphate	410 552	410 587	380 420	379 425

The above readings are in cubic centimeters draining from the bottom opening of a modified Schopper Riegler freeness tester as described in volume XCI—No. 9 of the Paper Trade Journal, August 28th, 1930 in an article written by Robert M. Boehm, using a bottom orifice of 9/64" opening.

In these illustrations there will be noted the great amount of variation between different brands in the same competitive grades. For instance, the original freeness of untreated bleached sulphite was 440 c. c. on one sample and 583 c. c. on another sample, a difference of 143 c. c., which is greater than the difference in freeness obtained when treating the 440 c. c. pulp with 18% caustic, the difference in this particular case being only 60 c. c. as shown in the above tabulation.

Freeness may bear a certain corresponding relation to the capillary power of the fibres in a felted sheet but this is not necessarily so. This is shown by the following experiment:—

A standard brand of kraft pulp had an original freeness of 465 c. c. .2 c. c. of light mineral oil when dropped on the surface of a standard felted sheet required 2.8 seconds in order to be absorbed. After having been treated with 6% caustic soda this particular pulp had a freeness of 486 c. c. In other words, it was somewhat slower yet .2 c. c. of the same oil required only 1.5 seconds to be absorbed. The addition of 2% of copper salt, according to my invention, figured as copper oxide on the weight of the fibre, caused the freeness of my product to increase to 455 c. c. and the oil absorption rate was 1.6 seconds. This is given by way of illustrating that the qualities which may be desired in an absorptive paper cannot always be measured by a freeness test of the pulp to be used in such a paper. Freeness is a convenient measure of showing that something has happened to the physical characteristics of fibres but will not to any degree of certainty indicate whether the felted fibrous sheet will make a satisfactory finished product when saturated or partially saturated with asphalt, oil, gum, adhesive material or other saturants which may be used for making the desired commodity.

I have discovered variables which may be definitely controlled so that a satisfactory finished product may be worked out by varying one or

more of the substances used to change the physical characteristics of the fibres.

Another advantage of my process resides in the fact that by encasing the fibres in a substance, or by depositing on the fibres a substance, or by physico-chemical combination with cellulose fibres of a substance, which substance is heavier, or of greater specific gravity, than the cellulose, I improve the felt forming qualites of my fibres in that the fibres assume their relative positions of formation more readily for a given porosity of sheet. The general qualities required in an absorbent paper are, ease of felting formation, a high degree of porosity as indicated by the Gurley densometer and extreme bulkiness or lightness in weight for a given thickness and, of course, the fibres must not contain, i. e., must not have adhering to themselves, any natural capillary repellant which may work against ease of absorption of the saturant to be used.

Microscopic examination shows that when using a higher concentration of caustic soda, i. e., towards the upper limits of non-mercerizing strength say 7% to 8% solution at 78° F., and a lower ratio of accelerating or activating chemical, i. e., copper or zinc salt, say 2% copper oxide, based on the weight of the fibre, in order to obtain a certain freeness which might otherwise be obtained by using a lower strength of caustic soda, say 6% and a greater amount of accelerating or activating chemical, say 8% copper or zinc salt figured as CuO on the weight of the fibre, the resultant pulp from the first case shows a curled or kinked fibre more circular in cross-section and somewhat brittle, whereas the fibres in the second case are more ribbon like in appearance and consequently the kinkiness of the individual fibres in the second case have more of a hinged effect and greater capillarity than when a higher strength of caustic soda is used. In other words, the fibres are kinked with caustic soda solution of less than mercerizing strength in combination with a physico-chemical activator or accelerator of non-mercerizing activity without materially changing the cross-sectional ribbon-like shape of the fibre but cause a series of retroversions or inclines and anticlines or hinged convolutions or sinuous formation along the fibre length.

The accompanying enlarged drawing represents Swedish kraft pulp treated with 6½% caustic soda and an amount of copper sulfate equivalent to 10% of CuO based on the weight of the fibre. The freeness of the pulp before treatment was 798 c. c. and after treatment was 424 c. c., which is approximately the same change in freeness as would be effected by an 18% caustic soda solution under similar conditions of temperature and mechanical treatment.

The specific gravity of cellulose fibre varies somewhat but is generally accepted as being approximately 1.4. The specific gravity of cupric hydroxide is approxmately 3.4. It will therefore be seen that by the deposition of copper hydroxide on the fibres or by the encasing of the fibres in copper hydroxide or by the physico-chemical combination with cellulose fibres of copper hydroxide, the specific gravity of the fibres will be materially increased because of the fact that the specific gravity of copper hydroxide is nearly two and one-half times that of cellulose. For this reason in the forming of a felted product, the encased fibres in water suspension gravitate quickly toward the supporting and forming medium of a felt forming machine, permitting a quicker and more thorough web formation which is less easily disturbed in the relation of the position of the felted fibres one to another than is the case with pulps which tend to float or carry in suspension more easily than my product. Of course, my encased fibres will gravitate more rapidly toward the felt forming medium of a freeness tester than will fibres not encased with a heavy substance, and will make for greater resistance to water passage and a slower freeness test as indicated by a larger volume of discharge from the bottom opening. This explains why the relation of freeness to capillarity is different in my product than in a product treated with caustic soda of mercerizing strength.

By treatment with a caustic soda solution of non-mercerizing activity I am able to produce a resilient felting pulp with minimum shrinkage of raw material as will be shown by the following example.

A sample of kraft pulp was shredded and divided into two portions. One was treated with approximately 18% of caustic soda solution and the yield of finished pulp with 84.1% of the weight of the original pulp used. The other portion of the pulp was treated with between 6% and 7% strength of caustic soda solution in which was mixed an amount of copper salt equivalent to 8% of the weight of the fibre. The freeness of the two samples were practically identical, whereas the yield in the case where the copper was used was 90.5% of the weight of the original pulp used. Where a large tonnage of fibre is to be processed the economic advantage of the nearly 7% gain in finished product for a certain weight of initial material used may be readily seen.

The brittleness of fibres treated with a caustic soda solution of high mercerizing activity tends to cause a large amount of fibre breakage resulting in high shrinkage in the conversion of pulp to paper and also causing a large amount of fines or comminuted matter which may stay in suspension until the last of the water drains from the sheet, thereby causing a "skin of fines" on the surface of the felted sheet. These "fines" may cause a filtering out of impregnating material which is a very serious disadvantage from an impregnating or saturating standpoint. My product tends to avoid this for two reasons:—

In the first place, a large amount of mechanical refinement is not necessary because of the higher specific gravity of my product because this permits sheet formation with a relatively small amount of water, and in the second place, my product is more susceptible to "hydration" or "slowing" than a product of equivalent freeness which has been produced by the use of a caustic soda solution of mercerizing strength.

The cooperative curling action of the caustic alkali and copper is evidenced by the fact that subsequent washing with copper solvent partially uncurls the fibres. As a matter of fact, complete removal of the encasing material from the fibres while in pulp form, i. e., before the relative position of the fibres become definitely fixed, will defeat an intended purpose of producing a bulky absorbent finished product.

The metal salt deposit on the fibrous pulp is allowed to remain on the fibre, providing a fibre encasing and preserving effect.

I have discovered that if the metallic salt deposit be removed from the formed felt by a solvent of that salt, an absorbency and porosity of felt will be obtained greater than would be obtained were the metallic salt removed from the

fibres before felting. This is due to the fact that the voids in the felt are produced while the interlocked fibres are in a maximum curled condition. The subsequent removal of the metallic salt or fibre encasing and curling agent partially uncurls the individual fibres but does not disturb the interlocked relation nor substantially change the voids.

Of the salts of electro-positive metals which may be used with caustic soda of less than mercerizing strength as an activating agent in producing absorbent, resilient felts, copper salts are the most active and cheapest. However, it may be that in certain cases, where high absorbency, capillarity, bulkiness and pliability may be desired, the color imparted by copper will be undesirable and acid washing may change the physical characteristics of the product more than may be desirable. In such a case, the copper may be supplanted in the fibre by a salt of aluminum, zinc or other more desirable metal than copper and the copper washed out. This is done by treatment of the copper crinkled pulp with aluminum sulphate or zinc sulphate solution in an amount approximately molecularly equivalent to the copper present in the product, without appreciably affecting the mechanical characteristics of the product and with the complete removal of any undesirable color. It amounts to the supplanting of the copper in cellulose combination by a metal compound which has less curling activity in association with caustic soda than copper. By this supplanting method, a metal compound is continuously in contact with the cellulose fibre so as to retard any tendency to uncurling of the fibre. This substituted metal compound will not materially affect the copper curled physical characteristics of the product, except as to color. This supplanting method is equally applicable to curled or non-curled fibre as a method of providing an encasement or colored encasement.

A method of preserving the curling of the fibre and, at the same time, coloring the fibres is to cause a chemical change in the metallic salt on the surface of the fibre which chemical change may also involve a change in color. This may be by means of a precipitating chemical, for instance, sulfides, which, reacting on copper curled fibres, will precipitate on the fibre surface a rich brown color without uncurling the fibres. This may take place either before or after felting, the metallic salt deposit not being removed from the surface of the fibre but being changed chemically and in color.

Various color combinations may be worked out by using other chemicals such as ferro and ferri cyanides, thiocyanates, oxidizing agents such as peroxides, permanganates, and reducing agents other than the sulfides aforementioned.

These various combinations may be made up to develop brown, yellow, green, blue, violet and red shades with various intermediate shades between these.

Broadly considered, the coloring takes place without changing the condition of the fibre, i. e., whether curled or uncurled, and the coloring may be changed, if desired, on uncurled fibre by a similar method.

In my Patent No. 1,830,131 I mention the use of caustic soda solutions of greater than mercerizing strength such as may be derived from the strong liquors of the causticizing operation of a soda pulp mill, i. e., up to 16% caustic soda solution and treating pulp in a kneader in a non-fluid mass, i. e., over 10% density. I have found it to be desirable that the freeness of pulp in process of production be quickly stepped up or stepped down in order to compensate for unavoidable temperature changes and for unavoidable delays in mechanical processing and for other reasons such as a too slow or too rapid quenching or stopping off of the curling action with the strong caustic according to such patented process. For continuous operation the method outlined in my Patent 1,830,131 requires the storage of considerable amounts of caustic soda solution made up to a definite strength. The freeness of the pulp in a downward or decreasing direction, that is, the slowing of the pulp may be readily controlled either by dilution of the caustic soda solution or by heating. The control of the freeness in the opposite or increasing direction is more difficult and expensive due to the fact that heretofore this might only be accomplished by refrigeration or by fortification of the entire volume of treating solution with extremely strong caustic. I am able by the addition of as little as ¼ of 1% of copper and zinc salt solution to a mass of fibre being treated with 16% caustic to change the freeness by a range which would ordinarily compensate for any anticipated variations due to the above mentioned causes.

The reaction between cellulose fibre and the copper or zinc salt and caustic solution mixture is extremely rapid. When using dry sheet pulp the rapidity of the reaction may cause a gelatinization of the sheet mass, thereby effecting impermeability and inability of the solution to surround and treat the individual fibres. I have overcome this difficulty in the following manner:—

A copper or zinc salt solution is added to caustic soda solution of the desired treating strength thereby causing a precipitate of copper hydroxide. This mixture of caustic soda and copper or zinc hydroxide suspension is added to the pulp or the pulp is added to this mixture to make up the desired density of mix and the whole is agitated until the fibres are disintegrated. Thereafter the copper or zinc hydroxide which is intimately mixed in the fibre mass is thrown into solution by the addition of a solvent such as Rochelle salts, sugar or other copper or zinc hydroxide solvent. The copper or zinc and caustic soda reaction on the fibre starts immediately.

Another method is to make a wet mix of copper hydroxide and fibre. When thoroughly and homogeneously intermixed the mass is dropped into a solution of caustic soda and copper hydroxide solvent and the whole is thoroughly stirred.

Another method is to mix thoroughly disintegrated pulp fibres with a sufficient volume of the treating chemicals in water, that the whole may be quickly stirred in a manner to surround and treat each fibre simultaneously with both accelerator or activator and curling agent.

Another method which has given excellent results is to intermix the fibres with caustic soda and after such treatment to discharge the pulp and caustic mass into a copper or zinc salt solution of such strength that the resultant caustic, fibre and copper or zinc salt mix shall be a substantially fluid mass, i. e., less than about 10% density or consistency of fibre. Of course, if agitation is sufficiently rapid and thorough a resultant non-fluid mass would be workable, i. e., over 10% density.

This method has several advantages.

1. The caustic solution strengths indicated herein in connection with the copper treatment are weak enough so that rapid disintegration of fibre masses into separated fibres readily takes place, without the formation of difficultly handled and slimy hemicellulose compounds in amounts or concentrations sufficient to interfere with continuous operation.

2. The less than mercerizing strength caustic treating solution dissolves organic substances from the fibres which dissolved substances act like sugar and Rochelle salts in holding the copper hydroxide in solution.

I have found that a solution made up as of the strength mentioned by Cohn in Patent No. 655,855, 9° Bé. at 100° C., using copper in the mixture equivalent to 7% of the weight of the fibre, figuring the copper as copper oxide and carried out at 78° F. will give a freeness effect greater than a 20% caustic solution under the same conditions of pulp suspension and mechanical treatment.

With my improved method, when using a copper or zinc salt, it is not necessary to use as great a strength of caustic solution as Cohn shows, nor is it necessary to raise the temperature above ordinary room temperatures, in order to produce the absorbent felt product described by Cohn, and to produce an absorbent felt product of markedly improved characteristics.

Cohn describes a material which will receive and keep impressions. This is because he does not compress the curled fibres in the wet state or the dry state in processing from pulp to felt. Cohn expressly eliminates any press roll or suction device from the Fourdrinier machine. If Cohn's fibrous material is partially compressed by paper machine press rolls in the wet state, or in the dry state, the resultant material will be resilient and springy and of high capillarity but these characteristics will still not be nearly as marked as in the product according to my method. I prefer to compress my product to secure the resilient and springy effect, and by my method to more distinctly control and regulate these characteristics to a marked degree, as an improvement upon Cohn.

In order to make the copper or zinc salt effective in the curling operation it is only necessary to hold the copper hydroxide in solution in the presence of the caustic soda or caustic lye, or to add a copper or zinc salt solution to the mixture of caustic and fibre. Copper hydroxide has an affinity for cellulose fibres and attaches itself to the fibres in the presence of caustic soda under the hereindescribed conditions to give the copper salt encased fibre with the unusual properties described.

The fibres must be separated and each subjected to the action of the solution by mixing so that an impenetrable gel will not form on the outside of the entire fibrous mass and prevent access of the solution to the individual fibres within the mass.

The present invention therefore involves rendering the individual fibres more susceptible to curling by chemical or physico-chemical encasement of the fibres by employing a chemical or physico-chemical encasing or combining agent for the fibres.

The copper or zinc hydroxide may be prepared by starting with metallic copper or zinc and an acid, or by making a solution of copper or zinc salt such as copper or zinc sulfate. If copper hydroxide is used, holding the copper hydroxide in solution in the presence of the caustic may be accomplished in a number of different ways, among which may be mentioned, the addition of Rochelle salts, sugar, or, the copper hydroxide may be taken up in a 30% to 40% caustic solution and the whole afterwards diluted. It is necessary to figure the copper compound, or zinc if used, on a different basis from the caustic because the copper or zinc is withdrawn and deposited on the fibre and must therefore be figured on the basis of the weight of the fibre to be treated and not on the basis of the strength or concentration of the copper in the solution. The caustic lye or caustic soda on the other hand must be figured on the basis of concentration of solution. In other words, the less the consistency or density of the pulp and chemical solution mix, the less will be the concentration of the copper salt solution. The concentration of the caustic lye solution may be kept constant for a definite grade of product regardless of the density or consistency of the pulp and solution mix (up to 15% density). In this connection reference is made in my copending application Serial No. 561,242, filed September 4, 1931, and hereinafter mentioned, to the retarding of the desired curling effect in using a pulp mix above a density of about 15% pulp to 85% treating solution. A mix above this density requires a caustic solution of increased concentration in order to secure the desired curling effect.

The following examples show the approximate ratio of parts by weight of copper compound, caustic soda, and fibre in mixes of 2%, 5%, and 10% density:—

2% Density mix

Analysis of mix:

2 parts fibre by weight	14
97.86 parts 7% caustic solution=97.86 parts × .07=6.85 parts NaOH	49
.14 of 1% CuO	1

Approximate ratio—CuO:NaOH:fibre=1:49:14

5% Density mix

Analysis of mix:

5 parts fibre by weight	14
94.65 parts 7% caustic solution=94.65 parts × .07=6.63 parts NaOH	19
.35 of 1% CuO	1

Approximate ratio—CuO:NaOH:fibre=1:19:14

10% Density mix

Analysis of mix:

10 parts fibre by weight	14
89.3 parts 7% caustic solution=89.3 parts × .07=6.25 parts NaOH	8.9
.7 of 1% CuO	1

Approximate ratio—CuO:NaOH:fibre=1:8.9:14.

In the preceding examples only one ratio of copper to pulp has been shown, namely, one to fourteen. It will be realized that the effects of the combinations shown are of degree and the invention covers any effective combination of non-mercerizing strengths of caustic soda and activating agents at any practical operating temperature when used with metallic salts such as copper and zinc. Also as a control method with caustic of mercerizing strengths.

The fibre curling drasticity of a mixture containing only 5% caustic soda with 2% on the weight of the fibre of copper oxide gives a curling effect at least equal to a 10% caustic soda solution.

A mixture containing 5% of caustic soda, 1⅓% copper oxide on the weight of the fibre and ½ of 1% zinc oxide on the weight of the fibre is still more reactive in curling fibre than where only the copper oxide is used with the less than mercerizing strength of caustic solution.

The bending or crinkling of the fibres tends to decrease the parallelity of fibre juxtaposition upon which the paper products of pulp depend for part of their tensile strength. It has long been the custom of paper makers to increase the strength of their sheeted products, when desired, by the use of mucilaginous substances, such as glue, starch, casein, or silicate of soda or by mechanically producing a mucilaginous gel from the cellulose itself. While the strength of my finished product may be increased by any of these well known means, I have discovered that the uniform distribution of copper compound attached to the fibres presents a unique means of strengthening the sheet during or after sheet formation.

According to my method the copper impregnated fibrous sheet is treated during formation or after formation with an amount of ammonia or ammonia compound chemically sufficient to form cuprammonium with the copper compound associated with the fibres. As is well known cuprammonium is a solvent of cellulose forming, in concentrated solutions, a sticky liquid. It may be seen that with insufficient water present to wash this sticky solution away and with the combination of my copper compound impregnated fibres, and the application thereto of ammonia and mechanical pressure and drying, such as obtained in the paper making process, there will result a gluing together of the fibres which will show up in the finished product in increased tensile strength. In any case, of course, the pulp product is washed to approximate neutrality before the felting operation, in accordance with the usual practice.

Reference is made to my copending application Serial No. 561,242, filed September 4, 1931, for Method of producing absorbent or resilient felt, in which treating solutions of some of the same chemicals are set forth in connection with the treatment of partially bruised fibres, and which treating solutions in that case may be less drastic or of less fibre curling reactivity than ordinary or usual treating solutions as set forth in that specification.

I am fully aware that solutions of caustic soda have been used for many years for the purpose of reacting with the acid cementaceous intercellular materials which nature has provided to bind together the cellulose fibres of wood and other vegetable substances.

It is not the purpose of this invention to perform the preliminary pulp producing operation of neutralizing and dissolving these cementaceous substances but rather to take cellulose fibres which have been previously separated and cleansed by any of the well known chemical processes and to treat these fibres as herein described for the purpose of presenting a product different from that produced by any of the usual pulp producing processes namely, the soda process, the sulfite process, the mono-sulfite process or the sulfate or kraft process.

The curling and kinking disfiguration of the finished or prepared fibres according to the process hereindescribed so reduces the overall length of the fibres as to preclude any possibility of spinning threads or weaving textile fabric therefrom.

Reference is made to my copending application Serial No. 558,826, filed Aug. 22, 1931, for Method of producing absorbent or resilient felt.

I claim:

1. The hereindescribed process comprising treating artificially curled or kinked copper compound impregnated cellulose fibres with an ammonia compound to form a mucilaginous coating on the fibres simultaneously with the production of the felted sheet so that a finished product of increased strength is formed.

2. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability, and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibres from which cementaceous, intercellular substances have previously been removed, and treating said fibres with caustic soda solution of non-mercerizing strength, together with a metallic compound of non-cellulose dissolving characteristics and of non-mercerizing effect, thereby forming a chemical or physico-chemical encasement or coating deposit which fixes or sets the fibers as to shape, the combined treatment with said caustic soda and metallic compound being carried out under elevated temperature such as to prevent curling or kinking of the fibers, and said combined treatment being of such character as would otherwise kink or curl the fibers, washing out the water soluble substances, and felting the fibers into a web on a paper making machine, substantially as described.

3. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability, and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibers from which cementaceous, intercellular substances have previously been removed, and treating said fibers with caustic soda solution of non-mercerizing strength, together with a copper compound of non-cellulose dissolving characteristics and of non-mercerizing effect, thereby forming a chemical or physico-chemical encasement or coating deposit in the form of a copper compound which fixes or sets the fibers as to shape, washing out the water soluble substances, felting the fibers into a web on a paper making machine, and treating the felted product with ammonia to provide a mucilaginous binder of cupro cellulose, substantially as described.

4. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability, and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibers from which cementaceous, intercellular substances have previously been removed, and treating said fibers with caustic soda solution of non-mercerizing strength, together with a copper compound of non-cellulose dissolving characteristics and of non-mercerizing effect, thereby forming a chemical or physico-chemical encasement or coating deposit in the form of a copper compound which fixes or sets the fibers as to shape, washing out the water soluble substances, treating the encased fibers either before or after washing with another metal compound to supplant the copper compound on the fibers without changing the set shape of the fibers, and felting the fibers into a web on a paper making machine, substantially as described.

5. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability, and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibers from which cementaceous, intercellular substances have previously been removed, and treating said fibers with caustic soda solution of non-mercerizing strength, together with a copper compound of non-cellulose dissolving characteristics and of non-mercerizing effect, thereby forming a chemical or physico-chemical encasement or coating deposit in the form of a copper compound which fixes or sets the fibers as to shape, washing out the water soluble substances, treating the encased fibers either before or after washing with another metal compound to supplant the copper compound on the fibers without changing the set shape of the fibers, the said other metal compound being a salt of zinc, aluminum or other metal which will supplant copper, and felting the fibers into a web on a paper making machine, substantially as described.

6. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability, and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibers from which cementaceous intercellular substances have previously been removed, and treating said fibers with caustic soda solution of non-mercerizing strength and of non-kinking effect alone, together with a copper compound of non-cellulose dissolving characteristics and of non-mercerizing effect, and of non-kinking effect alone, to produce a curling or kinking of the fibers without materially changing the cross-sectional ribbon-like shape of the fibers while causing a series of retroversions or inclines and anticlines or hinged convolutions along the fiber length, and forming a chemical or physico-chemical encasement or coating deposit in the form of a copper compound which fixes or sets the fibers in such flat ribbon-like curled and kinked shape, washing out the water soluble substances, treating the encased fibers either before or after washing with another metal compound to supplant the copper compound on the fibers without changing the set shape of the fibers, and felting the fibers into a web on a paper making machine.

7. The hereindescribed process of securing the desired characteristics of absorbency, capillarity, pliability and bulkiness of a felted paper product of cellulosic fibrous material, comprising employing finished or prepared cellulose fibers from which cementaceous, intercellular substances have previously been removed, and treating said fibers with caustic soda solution of non-mercerizing strength, together with a metallic compound of non-cellulose dissolving characteristics and of non-mercerizing effect, thereby forming a chemical or physico-chemical encasement of coating deposit which fixes or sets the fibers as to shape, the combined treatment with said caustic soda and metallic compound being carried out under elevated temperature such as to prevent curling or kinking of the fibers, and said combined treatment being of such character as would otherwise kink or curl the fibers, washing out the water soluble substances, and felting the fibers into a web on a paper making machine, and removing the encasement or coating deposit from the fibres by means of a solvent of the encasing substance.

8. The method comprising treating finished or prepared paper-felting fibrous pulp with material to curl the fibers and to form an encasement of the individual fibers, and treating the individually encased and curled fibers with a material to change the color of the encased fibers, the said curling and encasing material including a metallic compound which is deposited on the surface of the individual fibers to form the encasement, and said material for coloring comprising one or more of the following: sulfides or other reducing agents; ferro or ferri-cyanides; peroxides, permanganates or other oxidizing agents; thiocyanates.

9. A fibrous paper-felting product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasement or deposit on the individual fibers being chemically combined with a material producing a desired color without changing the physical condition of the fibers, said material comprising a sulfide.

10. A felted paper product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasement or deposit on the individual fibers being chemically combined with a material producing a desired color without changing the physical condition of the fibers, said material comprising a sulfide.

11. A fibrous paper-felting product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasing substance containing a metal, and said encasing substance being combined with material producing a desired color without changing the physical condition of the fibers.

12. A felted paper product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasing substance containing a metal, and said encasing substance being combined with material producing a desired color without changing the physical condition of the fibers.

13. A fibrous paper-felting product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasing substance being a copper compound, and said encasing copper compound being chemically combined with material producing a desired color without changing the physical condition of the fibers.

14. A felted paper product comprising finished or prepared cellulose fibers individually encased in a substance of non-mercerizing strength but of greater specific gravity than the cellulose fibers, the said encasing substance being a copper compound, and said encasing copper compound being chemically combined with material producing a desired color without changing the physical condition of the fibers.

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