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MANUFACTURE OF TRANSPARENT SHEET MATERIAL

George A. Richter, Berlin, N. H., assignor to
Brown Company, Berlin, N. H., a corporation
of Maine

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This invention relates generally to the manufacture of transparent sheet material falling more particularly in the class of those containing cellulose as the base or starting material. An object is to make possible the manufacture of such sheet material from a paper base and the realization in the finished sheet material of a high degree of clarity or transparency such as occurs in pellicles of regenerated cellulose known as "Cellophane", as well as of other desirable qualities which exist only to a limited degree, if at all, in "Cellophane." Another object is to enable the manufacture of such transparent sheet material at a cost much lower than that of "Cellophane" or of other films or transparent sheet materials as have heretofore been produced. Still another object is the attainment of transparent sheet material having a combination of characteristics including high strength, folding endurance, flexibility, impermeability to fluids, etc., such that it is eminently suited for use as a wrapping material for goods or articles which are advantageously displayed and sold in a transparent envelope or as a wrapping material which protects edibles or other perishable articles against deterioration, and at the same time stands up well against the action of water, oils, fats, and other liquids and semi-solids which may be associated with such articles.

There are various paper products which possess some or all of the foregoing desired qualities to some degree. Thus, so-called glassine papers, vegetable parchment, vulcanized paper, and mercerized paper fall into this category, but all of these known products are translucent, that is, have so much "cloud" or residual opacity that they cannot compete for some uses with transparent sheet material such as "Cellophane." Of these products, glassine paper is perhaps the most widely employed because it can be manufactured comparatively inexpensively. Indeed, such paper is marketed at only a small fraction of the selling price of "Cellophane." It is, however, markedly inferior to "Cellophane" in such desired qualities as clarity and impermeability, even though it possesses a much higher tear resistance. Glassine paper is sometimes subjected to after-treatments with a view toward improving its clarity, but none of these treatments bring about a clarity coming close to that of "Cellophane."

I have found that it is possible to transform paper, and more especially paper which has been made translucent by suitable mechanical and/or chemical treatment, to a perfectly clear or transparent state similar to that of "Cellophane" by subjecting the paper to the action of suitable cellulose-gelatinizing media, arresting the gelatinization at the proper time, and setting the gelatinized cellulose in situ in the paper. I have fur-

ther found that while it is possible to use for this purpose such cellulose-gelatinizing agents as aqueous solutions of the alkali-thiocyanates, nevertheless it is distinctly preferable to use cuprammonium solutions for the reason that they can be made to act quickly and yet can be controlled in their action so as to keep the paper intact, particularly when the paper has been rendered dense and/or translucent by previous mechanical and/or chemical treatment. Thus, the gelatinizing action of cuprammonium solution on paper may be controlled by varying the concentration of the solution, its temperature, and the time of its contact with the paper. As already indicated, the paper employed as the starting material is preferably one which has been rendered translucent by mechanical and/or chemical treatment. For instance, glassine paper, parchmentized paper, vulcanized paper, mercerized paper, or the like, may constitute the starting material. In some instances, a paper which has merely been calendered or super-calendered to a dense condition, may be employed, for instance, a paper made from pulp which has not been beaten excessively as in the manufacture of glassine paper but calendered or super-calendered in the presence of moisture to a density approaching that of glassine paper. It is preferable that the paper employed be waterleaf, that is, free from non-cellulosic sizing and/or filling ingredients, although in some cases it may be desirable to incorporate into the paper suitable water-repellent materials, such as resins or waxes, which do not detract appreciably from the clarity desired in the finished sheet but which serve to enhance the quality of water-repellency desired therein. I have found that papers which have initially been rendered translucent by chemical treatment, such as parchmentizing solution (sulphuric acid solution or its equivalent), vulcanizing solution (zinc chloride solution or its equivalent), and mercerizing solution (caustic soda solution or its equivalent), are especially reactive toward a cuprammonium solution and can hence undergo the transformation desired in accordance with the present invention to good advantage. Indeed, even when a glassine paper or well-calendered paper has initially been prepared, it may be desirable to improve the reactivity of such paper toward cuprammonium solution by putting it through a parchmentizing, vulcanizing, mercerizing, or similar chemical treatment. From the standpoint of economy, however, glassine paper as such represents an attractive starting material, particularly when the glassine paper has undergone super-calendering in the presence of moisture so that maximum density has been reached therein. The fact is that the ordinary glassine paper of commerce responds nicely to the treatment with cupram-

monium solution and can be transformed without difficulty into the transparent sheet material of the present invention at a cost considerably lower than that entailed in the manufacture of "Cellophane." As is well known, glassine paper is prepared from cellulose pulp which has undergone drastic hydration or gelatinization in so-called stone-roll beaters. The highly beaten or gelatinized pulp yields a dense, tough, paper sheet, which under super-calendering action in the presence of moisture and heat acquires increased density and the translucency characteristic of glassine paper. The treatment with cuprammonium solution which such paper undergoes according to my invention evidently destroys such fibers or fiber fragments as remain in the pulp from which the glassine paper is prepared. In this connection, it is to be remarked that fibers or fiber fragments must be present in the pulp from which the glassine paper is prepared in order to get the desired speed and character of sheet formation on the paper-making machine, but it is these fibers or fiber fragments which cloud the paper sheet and/or give rise therein to air-cells and their attendant fog. The cuprammonium solution when applied according to the present invention evidently swells and gelatinizes the fibers and fiber fragments in the sheet and thereby does away with the air-cells or pores and the attendant fog in the sheet. The cuprammonium treatment also tends to destroy such surface irregularities as appear in the sheet, for instance, such marks as are caused in the paper by the forming "wire" or wire cloth on which the paper web is formed or by the felts with which the freshly formed web contacts in its course on the paper-making machine. In order to ensure a perfectly smooth surface in the finished papers of the present invention, it may be desirable to prepare the paper base on a Fourdrinier machine, whose forming wire is of extremely fine mesh, or on a cylinder machine whose cylinder mold is covered with finely woven wire cloth or similar reticulated base which leaves little, if any, impression upon the web of paper formed thereon.

The process of the present invention includes a number of steps supplementing that of treating the paper base with the cuprammonium solution. Assuming that the proper paper base has undergone suitable treatment with cuprammonium solution as the first step, the second step is that of arresting the reaction by setting or regenerating the cuprammonium cellulose in situ in the paper as by treatment with a solution of caustic soda or equivalent alkali. The caustic soda or equivalent alkali liberates the ammonia from the cuprammonium-cellulose complex and this is accompanied by setting of the cellulose and the liberation of copper oxide in the paper sheet. The paper sheet is then preferably washed free of alkali or other water-soluble products as the third step of the process. The fourth step consists in removing the copper oxide from the paper as by treating the paper with a suitable acid reagent, e. g., a sulphuric acid solution, which functions also to complete the setting or regeneration of the cellulose. The acidified paper is then washed free of acid and finally dried as the fifth and sixth steps, respectively, of the process.

In order to indicate with greater particularity how the various steps of the process may be performed, as well as the modifications that might be made therein, each step will now be dealt with individually.

Step I.—The treatment with cuprammonium

solution may be carried out with a solution which has been prepared by dissolving 4 parts by weight of copper hydroxide in 100 parts by weight of 28% aqua ammonia. The solution may be kept at about 25° C., and the paper undergoing treatment may be immersed in such a solution for 3 to 60 seconds, depending upon the thickness of the paper sheet and its reactivity with the solution. It is, of course, possible to vary the temperature of the solution as well as the concentration of copper and ammonia therein. Indeed, it is possible to operate with solutions whose temperature ranges from below 0° C. to 50° C. by providing therein the concentration of copper and ammonia and an interval of reaction with the paper consonant with the desired modification of the paper. When operating at a temperature of say, 0° C., the cuprammonium solution may be one prepared from 4 parts by weight of copper hydroxide and 100 parts by weight of aqua ammonia of considerably greater than 18% strength because of the increased solubility of ammonia at such low temperature. On the other hand, when the cuprammonium solution is used at temperatures of say, 40° C. to 50° C., it is necessary to keep the solution under super-atmospheric pressure in order to realize therein an ammonia concentration and a reactivity approaching that attainable at say, 25° C. Otherwise, on account of the lower solubility of ammonia at such higher temperature, it becomes necessary to extend the period of treatment of the paper with the cuprammonium solution in order to realize reaction on the paper to a given degree. It is, of course, possible to maintain the cuprammonium solution under pressure and/or to increase its reaction period on the paper so as to offset the effect of temperature increase in the solution. The paper sheet may be immersed in a single bath of cuprammonium solution or it may be led as a continuous sheet through a number of baths of cuprammonium solution. The bath or baths of cuprammonium solution may advantageously contain sugar, glycerine or other suitable alcoholic agent, and wetting-agents, such as "Nekal B-X", which promote the penetration of the solution into the paper. Upon removal of the paper sheet from the solution, it may be squeezed free of excess liquor which may be returned to the bath of solution.

Step II.—The moist, partially gelatinized paper sheet containing residual cuprammonium solution is treated, preferably in unwashed condition, so as to cause a setting or regeneration of the chemically gelatinized cellulose associated therewith. While the desired result may be brought about by drying the paper under heat, treating it with hot water, with hot dilutions of various salts or other electrolytes, or with concentrated solutions of salts, or other electrolytes at room or other temperature conditions, it is preferable to use for this purpose caustic soda or equivalent alkaline solutions under the appropriate conditions of concentration, time and temperature. For instance, a bath of caustic soda solution of 5% strength may be used at a temperature of about 20° C. as the medium in which the paper sheet, fresh from its treatment with cuprammonium solution, is immersed for say, 3 to 20 seconds. Other conditions of treatment are possible, for instance, immersion in a bath of caustic soda solution of 30% strength at 50° C. for a 5-second period. The bath may be one containing potassium hydroxide or other suitable alkali in lieu of, or together with, the

caustic soda. It may be refrigerated to temperatures below, as well as heated to temperatures above that of the prevailing room temperature.

Step III.—The alkali-treatment of the paper sheet leaves a residue of alkali therein as well as hydrated copper oxide as a reaction product. At this stage, the sheet is still light blue in color, although of a fainter blue than that of the cuprammonium solution, but it has been rendered tough and of high wet strength, wherefore, it can well maintain its integrity when it is subjected to a washing operation to free it from alkali and other water-soluble products. The sheet is washed in water which may be at any suitable temperature, although hot water, say, at about 80° C. is evidently best for this purpose on account of its effectiveness in leaching out alkali from the sheet and in completing the work of setting the chemically gelatinized cellulose when setting has not previously gone to completion.

Step IV.—The washed sheet may be immersed in various solutions of acid and/or acid salts capable of extracting therefrom the hydrated copper oxide or other inorganic residues present therein. Thus, a 2% solution of sulphuric acid at 25° to 30° C. is quite satisfactory for this purpose. When the washed sheet is immersed in this solution, its copper oxide content is readily dissolved and removed as attested to by the fact that its light blue color quickly disappears and that it assumes the desired transparency, strength, and other qualities. Solutions of sulphuric acid and/or of sodium acid sulphate may be used under other conditions of concentration and/or temperature. The acid solution not only functions to dissolve the hydrated copper oxide present in the sheet and thereby to clear up the sheet, but also to complete the setting or regeneration of the chemically gelatinized cellulose, should such setting still be incomplete as the sheet enters the bath of acid solution.

Step V.—The acidulated sheet is washed free of acid solution with hot or cold wash water. The wash water may be rendered faintly alkaline with suitable alkalis, such as borax, to ensure neutralization and elimination of acid residues.

Step VI.—The washed, transparentized paper, which has the appearance of ordinary "Cellophane" and the usual films of cellulose acetate and cellulose nitrate, is then dried preferably under heat and pressure such as can be had in a photographic hot drying press or in a hot calender stack. The sheet is quite plastic before it is fully dried so that maximum density and clarity is ensured when drying is performed under heat and heavy pressure. In the case of a finished sheet wherein the quality of stretchability is desired, however, drying may be performed with little, if any, restraint of the sheet so as to permit partial or complete shrinkage thereof.

There are other miscellaneous features which may, in some instances, advantageously enter into the present invention. For instance, rather than using a previously prepared cuprammonium solution for treating the paper sheet constituting the starting material, copper oxide may be incorporated into the paper sheet as part of the paper-making process and the copper-oxide-filled paper may then undergo the action of aqua ammonia to form cuprammonium solution of the desired strength in situ in the sheet and thereby to effect the desired gelatinizing action on the sheet. The copper oxide may, for instance, be added in powdered condition and in appropriate

amount to the bulk paper-making pulp in the beater engine before it is run off on the paper-making machine. So, too, the finished sheet may have added thereto in the course of its manufacture suitable agents which improve its pliancy, water-repellency, and other qualities. For instance, such plasticizing agents as glycerine, ethylene glycol, or other polyhydric alcohol may be added thereto, as by way of the acid solution used in the fourth step or the wash water used in the fifth step, for the purpose of increasing its pliancy. Suitable water-repellent agents, such as oils and waxes of a transparent nature, may be added thereto during, before, or after the last step of drying. For instance, oil may be emulsified or wax dispersed in the wash water used in the fifth step so as to induce a penetration of these agents into the sheet particularly when subsequent drying is conducted at elevated temperature in a press or calender stack. In other instances, the dried sheet may be thinly coated with a suitable transparent, waterproofing material, such as the transparent waterproofing compositions used in coating "Cellophane" to produce so-called "moisture-proof Cellophane". The process of the present invention lends itself to continuity of practice when translucent or compacted papers of the character hereinbefore referred to are put through the baths of the various treating steps under the appropriate conditions. Indeed, I have found that by maintaining the baths under the appropriate conditions, they need not be of undue length to permit paper to be run continuously therethrough at speeds of say about 10 to 30 feet per minute and be delivered in the desired finished condition for drying. While paper as it issues from the dry end of a paper-making machine may undergo the processing of the present invention, nevertheless it is usually more expedient to carry on such processing independently of the paper-making machine, for instance, on a sheet of paper being progressively unwound from a roll or being progressively delivered from apparatus which handle rolls of paper, like the apparatus which do the work of parchmentizing, vulcanizing, mercerizing, or super-calendering paper, and are run at speeds similar to those at which the paper can be put through the process of the present invention. In running the paper continuously through the various treating baths, it is possible to effect a countercurrent treatment such as permits of a maximum recovery of chemicals. For instance, the washing operation constituting the third step may be performed by running the wash water through the bath in countercurrent flow to the movement of the sheet and at such a rate that the effluent wash water is of maximum concentration and can be used in large part for the preparation of the alkaline liquor constituting the setting or regenerating bath of the second step. Such alkaline wash water as cannot be used in the setting or regenerating bath of the second step may be used in preparing the faintly alkaline wash water of the fifth step. A similar principle may be used in the washing operation constituting the fifth step of the process, in which case it may be desirable first to wash with plain water to effect a maximum recovery of acid and then to carry out an independent second stage of washing with faintly alkaline wash water to ensure neutralization of the sheet. Part of the acid wash water cannot be reused in the fourth step, but must be removed from the system in order to avoid an undesirable accumulation of

copper sulphate in the acid bath of the fourth step. The removed acid wash water containing the copper sulphate may, however, be subjected to suitable chemical treatment designed to convert the copper sulphate into hydrated copper oxide for re-use in preparing fresh cuprammonium solution. Such countercurrent washing as has been described is particularly desirable when a strongly alkaline bath is used in the second step and a strongly acid bath is used in the fourth step for the purpose of effecting the desired reactions quickly, as it means that the desired end can be attained with minimum loss of chemical. The ammonia liberated during the performance of the second step may be recovered and re-used together with the regenerated hydrated copper oxide in the preparation of fresh cuprammonium solution. It is thus seen that the process of the present invention may be carried out quite economically from the standpoint of low chemical costs, as it presents the opportunity for easy recovery of considerable of the chemicals entering thereinto.

I have already indicated that the sheet coming from the last bath of wash water is preferably dried at elevated temperature in a press in the usual case, that is, when the finished sheet need not be stretchable. In processing a continuous sheet, such drying can be effected by leaving the sheet as it progressively issues from the last bath of wash water through squeeze rolls and thence through a so-called hog super-calender such as is employed in the glassine paper industry. The application of heat and heavy pressure conduces to the realization of maximum clarity in the finished sheet, inasmuch as the density of the sheet is maximized and air-cells in the sheet minimized thereby. Indeed, it may be desirable to subject the sheet to the action of squeeze rolls at various stages of the process, for instance, as it emerges from some or all of the treating baths, so as to foster the exclusion of air therefrom and maximum density therein.

I have already adverted to the fact that when the cellulose solvent is a cuprammonium solution, the cuprammonium solution may be prepared in situ in the paper by incorporating copper oxide as a filler in the paper and then treating such paper with ammoniated water. In some instances, copper oxide may be incorporated into the paper by impregnating it with solutions of copper salts, such as copper sulphate, and then precipitating hydrated copper oxide in situ in the paper by adding an alkaline solution, such as caustic soda, thereto, and washing the paper free of residual alkali. There are other cellulose solvents that might be used in accordance with my invention, depending upon the reactivity of the cellulose of the paper or the physical character of the paper. Thus, in connection with a translucent paper, such as glassine paper represents, it is possible to clear up the sheet considerably through the use of zinc chloride solution of the usual vulcanizing strength, or sulphuric acid solution of the usual parchmentizing strength, or equivalent reagents. The action of such reagents may be arrested and they may be removed by washing with plain water or water containing a slight amount of neutralizing agent. The mercerization of a glassine paper increases the reactivity of the cellulose toward vulcaniz-

ing, parchmentizing and similar reagents, and is hence to be desired as a preliminary treatment followed by washing and by the application of such reagents when a finished sheet of the best transparency is sought.

One of the advantageous qualities which distinguish my finished sheets from "Cellophane" even when they are made to possess a transparency similar to that of "Cellophane" is their superior tear resistance. While I cannot account precisely for their superiority in this respect, it appears that such superiority may be traceable to the fact that at no stage of my process does the cellulose of the paper base go completely into solution, whereas, in the manufacture of "Cellophane", cellulose is dissolved completely to form a solution from which the cellulose is precipitated or regenerated when the solution is cast as a film. The transparentized paper sheet which I produce evidently owes its transparency in part to the mechanically hydrated cellulose entering into the glassine paper which I preferably employ as the starting base and in part to the chemical gelatinization which it subsequently undergoes and which is controlled so as to swell the cellulose to the desired transparent state without putting it into complete solution.

I claim:

1. A process which comprises treating a copper-oxide-filled cellulose fiber sheet with ammoniated water to form in situ throughout the sheet a cuprammonium solution serving to convert the cellulose fiber into cuprammonium cellulose gel while maintaining the integrity of the sheet, chemically arresting the action of the cuprammonium solution and simultaneously precipitating chemically the cuprammonium cellulose gel in situ in the sheet to form regenerated cellulose and copper oxide removing the copper oxide from the sheet, and drying the resulting sheet.

2. A process of producing a substantially transparent paper sheet, which comprises impregnating a paper sheet consisting essentially of cellulose fiber with cuprammonium solution to gel the fibers while maintaining the integrity of the sheet, chemically arresting the action of the cuprammonium solution in the wet sheet and simultaneously setting the cellulose gel therein, removing the copper constituent from the wet sheet, and drying the sheet while thus wet and plastic under sufficiently heavy pressure between heated surfaces to develop substantial transparency in the resulting dried sheet.

3. A process of producing a substantially transparent sheet, which comprises impregnating a paper sheet consisting essentially of cellulose fibers with cuprammonium solution to gel the fibers while maintaining the integrity of the sheet, treating the sheet with a solution of alkali to liberate the ammonia from the cuprammonium-cellulose gel and to set the cellulose, dissolving the copper constituent from the wet sheet with an acid reagent, washing the sheet, and drying the sheet while thus wet and plastic under sufficiently heavy pressure between heated surfaces to develop substantial transparency in the resulting dried sheet.

GEORGE A. RICHTER.