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MANUFACTURE OF CHEMICALLY MODIFIED PAPERS

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

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This invention relates to the manufacture of papers of the class having increased density, translucency, wet and dry strengths, water-repellency, resistance to oils and fats, and other desirable qualities, as a result of a chemical modifying treatment which they have undergone. While not restricted thereto, the present invention comprehends such chemical modifying treatments as accomplish what is known in the art as parchmentization, vulcanization, and mercerization of the paper. Inasmuch as all the foregoing chemical modifying treatments are based upon the use of aqueous chemical solutions which effect more or less gelatinization of the cellulose constituting the paper, the action of such solutions will be hereinafter generically referred to as an incipient chemical gelatinization of the paper.

In manufacturing papers of the foregoing character, it has heretofore been the practice to start with a so-called waterleaf paper sheet, that is, a sheet substantially devoid of fillers or sizes, and to immerse such sheet in a bath of appropriate chemical solution under conditions of time, temperature, and chemical concentration to effect the desired gelatinizing action on the cellulose. The sheet is then washed free from chemical solution and dried. The commercial performance of such a process, which involves the handling of a continuous paper sheet under tension, must be carried out with careful control of the various treating conditions, since otherwise the paper, which has comparatively little strength when it initially enters into an aqueous solution, might be ruptured or torn before it acquired the enhanced wet strength accruing from sufficient exposure to the chemical solution.

In accordance with the present invention, regenerated cellulose is incorporated into a paper sheet which is to undergo parchmentization, vulcanization, mercerization, or analogous chemical transformation. Aside from the fact that regenerated cellulose is amenable to the same sort of chemical reaction or transformation as that effected upon the virgin cellulose of the paper base, it is a highly valuable ingredient in the paper base because it increases vastly the wet strength of such base and thus makes it possible to overcome the danger of rupturing or tearing the base even when it is passed as a continuous sheet through an aqueous chemical solution or wash water under conditions which would give rise to the rupture or tearing of the usual paper base. It is thus seen that by following the principles of the present invention, it is possible to do away with the troubles heretofore encountered in making parchmentized, vulcanized, and mercerized paper sheets, and at the same time to realize the desired qualities of density, translucency, wet and dry strength, water-repellency, grease resistance, etc., in the finished sheets. Indeed, it becomes possible through the practice of my invention to carry out steps which could heretofore be performed only with difficulty. For instance, if it were attempted to parchmentize, vulcanize, or mercerize the ordinary paper base only locally by a continuous process, trouble would be apt to crop up during the subsequent washing operation, as the untreated portions of the paper would become soft and weak when exposed to the wash water and hence tend to disintegrate. On the other hand, a paper which has preliminarily been reinforced by regenerated cellulose in accordance with the present invention, may undergo only a localized chemical treatment and yet withstand disintegration during washing on account of the high wet strength of such paper even at its chemically untreated portions. For instance, a continuous sheet of paper containing regenerated cellulose may receive the chemical treating solution from a roll similar to the usual printing roll, as in the form of an ornamental design, letters, words, or other desired characters or impressions, whereupon, the locally treated or impressed paper may be passed through a bath of wash water and thence over a bank of drying drums or other suitable dehydrating equipment. When the paper is treated locally as with parchmentizing, vulcanizing, and mercerizing solutions, the conditions maintained may be such as to produce thereby a puckered or crinkled effect which may be considered desirable as ornamentation. This effect arises from the fact that such reagents induce appreciable shrinkage of the paper and, when such shrinkage is permitted to proceed unrestrained, is accompanied by a puckering or crinkling of the paper. The extent to which puckering or crinkling will take place depends upon various factors, principal of which is the tension under which the paper is treated and which may be such as to permit complete, partial, or practically no shrinkage. In some instances, a localized chemical action may be had by protecting the paper containing the regenerated cellulose against such action with suitable water-repellent or sizing materials, such as glue, gums, rubber latex, or the like, at those areas which are to serve as a contrasting back-

ground for the effect realized by the localized chemical action. Such sizing materials may be applied according to the desired predetermined pattern to the paper from a roll similar to the usual printing roll and then set or dried in the paper. When such paper is then subjected, as by immersion, to the action of a parchmentizing, vulcanizing, or mercerizing solution, only the unsized localities will readily respond to such treatment, wherefore, only such localities will show distinctly the effect of such treatment. In such instance, too, the paper containing the regenerated cellulose will resist disintegration at its unsized localities by virtue of its high wet strength not only against the action of the chemical treating solution, but also of the wash water to which it is subsequently subjected and which might tend to rupture the sized areas, unless they were reinforced in wet strength by regenerated cellulose. It is possible to incorporate the regenerated cellulose into the paper at the same time as the sizing material only over those areas which are to resist the action of the chemical treating solution. Thus, a mixture of viscose and glue solution or a mixture of viscose and rubber latex may be used for such purpose. Ordinarily, however, it is more expedient and satisfactory to associate the regenerated cellulose throughout the paper and then to apply the sizing material independently to the paper over those areas which are to be protected against the action of the chemical treating solution.

The paper base employed for the purposes of the present invention may be fabricated from various kinds of cellulose fiber including cotton or linen rags, chemical wood pulps, such as sulphite, kraft and soda pulp, refined wood pulp, or the like. The cellulose fiber used as raw material may be used in substantially unbeaten condition or it may be beaten to the desired extent or otherwise suitably conditioned for the paper-making operation. The regenerated cellulose may be associated with the paper in the course of paper manufacture or after paper manufacture has been completed. While various cellulose derivative solutions, such as a cuprammonium cellulose solution, might be used as the source of regenerated cellulose, it is preferable to work with viscose for the sake of economy. The cellulose may be regenerated from the viscose through the use of various regenerators, such as alum, acetic acid, or other acid or acid salt solutions. As already indicated, this may be effected at any suitable stage of paper manufacture, for instance, in the bulk paper-making stock preparatory to its delivery to the paper-making machine, or in the freshly formed web on the paper-making machine, or in the dry web issuing from the drier drums of the paper-making machine. The amount of regenerated cellulose incorporated into the paper may be varied, depending upon the characteristics desired therein. For instance, when it is desired that the paper be highly absorptive and quickly penetrable by chemical treating solution, as little as ½ to 2% regenerated cellulose may be present therein. Paper containing such a small amount of regenerated cellulose is practically as absorptive as the ordinary waterleaf paper base. In some instances, the absorptivity of the paper base containing the regenerated cellulose may be increased through the inclusion therein as a paper-making ingredient of a small amount of suitable wetting-out agent, such as "Nekal B-X". On the other hand, in some instances, it may be desirable to slow down the influx of chemical solution into the paper. This may be done by raising the amount of regenerated cellulose in the paper and/or by introducing along with the regenerated cellulose a suitable sizing agent, such as rosin, paraffin wax, or the like. The sizing agent may, if desired, be added in admixture with the viscose to the paper-making stock or to the paper. For instance, an aqueous dispersion of paraffin wax stabilized by rosin soap or other hydrophilic colloid may be admixed with the viscose and then be precipitated at the same time that the cellulose is regenerated in the paper-making stock or in the paper. To this end, a single chemical, such as alum, may serve the purpose of breaking down the paraffin dispersion as well as of regenerating the cellulose from the viscose.

A paper sheet containing regenerated cellulose and produced in any one of the many ways hereinbefore outlined may then be put through the desired incipient chemical gelatinizing treatment. For instance, it may undergo the usual parchmentizing treatment with sulphuric acid solution, then be washed, and finally dried to produce a translucent sheet characterized by its high density, excellent wet strength, and resistance to the penetration of oils, fats, and the like. The resulting parchment paper may be glycerinated, as ordinarily, to acquire greater softness and flexibility, particularly when it is to be used for wrapping foodstuffs. So, too, the paper containing regenerated cellulose may be subjected to the conventional vulcanizing treatment with zinc chloride solution, then be washed, and finally dried. Vulcanization, as is well known, also increases the density and hardness of the paper sheet and renders it resistant to the softening and weakening action of water and to the penetration of oils, fats, and the like. In some instances, it may be desirable, according to the present invention, to produce from papers containing regenerated cellulose so-called "hard fiber" such as is satisfactory for use as panelboard or as the material from which such articles as ice cream plates, ice cream spoons, or the like, are fabricated. Thus the procedure may be one of applying the vulcanizing solution of zinc chloride to a comparatively thin sheet of paper containing regenerated cellulose and of laminating the sheet to the desired thickness. A board of the desired thickness may, for instance, be made by convoluting the freshly vulcanized, wet sheet on a drum or other suitable form. The laminated board, whose wet plies tend to bond intimately with one another, may be stripped from the form, washed, and finally dried. Finally, papers containing regenerated cellulose may, according to the present invention, undergo treatment with a solution of alkali under mercerizing conditions such as would be apt to cause the ordinary waterleaf paper sheet to go to pieces. The mercerizing treatment employed in connection with the present invention may be performed as ordinarily under room temperature conditions with a caustic soda solution of about 18% or greater strength. It is, however, possible to realize the desired mercerizing action on the paper sheet through the use of caustic soda solutions of less than 18% strength, provided that the solution is maintained at a sufficiently reduced temperature. Indeed, mercerization may be had with caustic soda solutions of as low as 1 to 5% causticity when such solutions are refrigerated to a sufficiently

low temperature, for instance, to a temperature sufficiently below zero to cause ice crystals to separate out of solution and to raise the concentration of alkali to a considerable extent in the unfrozen portion of the solution. In this connection, it is to be remarked that whereas an ordinary waterleaf paper sheet softens and weakens quickly and marked in dilute caustic soda solutions, particularly when they are refrigerated to temperatures considerably below room temperature (20° C.), and hence invariably disintegrates under slight provocation in such solution, a paper sheet containing regenerated cellulose can effectively withstand such treatment. The incipient or partial chemical gelatinization desired in accordance with the present invention may be had through the use of solutions of alkali-thiocyanates and other known reagents, but I have dealt more specifically with the use of parchmentizing, vulcanizing, and mercerizing solutions because they are of greater commercial importance.

The various chemical treatments hereinbefore outlined all have the effect of incipiently gelatinizing the cellulose fiber constituting the paper base, with the result that the paper base becomes harder, denser, and more resistant to degradation by such liquids or semi-solids, as water, oils, fats, and the like. The gelatinized cellulose generated by such chemical treatments evidently enters into the pores and interstices of the paper wherein it serves to bond together more tenaciously the cellulose fibers as well as to reduce the air carried by the paper and its attendant opacity. The fact is that in comparatively thin papers, the air content may be cut down to such an extent that the paper acquires the familiar translucent or semi-transparent state. The value of associating regenerated cellulose with paper prior to such chemical treatments, as herein disclosed, lies in the fact that the regenerated cellulose not only confers upon the paper the ability to maintain its integrity when it first contacts with the chemical treating solution, but also that it does not interfere with the realization of qualities sought in the finished paper. Thus, the regenerated cellulose does not militate against the realization in the finished paper of such qualities as translucency, high density, resistance to softening and weakening action of water, and to the penetration of oils, fats, etc. On the contrary, the regenerated cellulose appears to enhance such qualities in the finished paper, which enhancement may be attributable to the ability of the regenerated cellulose to undergo reaction with the chemical modifying solution in the same way as does virgin cellulose fiber and perhaps even more rapidly on account of its fine state of distribution throughout the paper.

I claim:—

1. A process which comprises preparing a paper containing virgin cellulose fibres and about ½ to 2% regenerated cellulose, and then subjecting such paper to the action of a chemical solution under conditions to effect an incipient chemical gelatinization of the regenerated as well as the virgin cellulose content of the paper.

2. A process which comprises preparing a paper containing virgin cellulose fibers and about ½ to 2% regenerated cellulose, and then parchmentizing such paper, thereby similarly chemically modifying both the regenerated and virgin cellulose contents of the paper.

3. A process which comprises preparing a paper containing virgin cellulose fibres and about ½ to 2% regenerated cellulose, and vulcanizing such paper, thereby similarly chemically modifying both the regenerated and virgin cellulose contents of the paper.

4. A process which comprises preparing a paper containing virgin cellulose fibres and about ½ to 2% regenerated cellulose and then mercerizing such paper, thereby similarly chemically modifying both the regenerated and virgin cellulose contents of the paper.

5. A process which comprises associating a mixture of viscose and dispersed paraffin wax with paper, treating the paper with a single chemical solution to regenerate the cellulose from the viscose and precipitate the wax from the dispersion in the paper, and subjecting the paper to the action of a chemical solution under conditions to effect an incipient chemical gelatinization of the regenerated as well as the virgin cellulose content of the paper.

6. A process which comprises associating a mixture of viscose and dispersed paraffin wax with paper, treating the paper with an alum solution to regenerate the cellulose from the viscose and to precipitate the wax from the dispersion in said paper, and subjecting the paper to the action of a chemical solution under conditions to effect an incipient chemical gelatinization of the regenerated as well as the virgin cellulose content of the paper.

GEORGE A. RICHTER.