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PROCESS FOR OBTAINING CELLULOSE FROM RESINOUS PINE WOODS

Francesco Carlo Palazzo, Firenze, Italy; vested in the Alien Property Custodian

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As is known the maximum part of the wood cellulose is produced chiefly in view of being utilised in the rayon industry, by the calcium bisulphite process, but the extension of this industry hitherto has been affected by a limiting factor, namely the availability of coniferous timbers poor in resins such as those of the various species of fir, since the application of that process, even in its more modern forms, has hitherto remained circumscribed to such woods, without being able to extend to all the various species of pines. In particular the red fir or Scotch pine (*pinus silvestris*) which is so widely diffused in central and northern Europe and the cluster pine or pinaster (*pinus pinaster*), which forms extensive forests, chiefly in France, in the Department of the Landes, have not been able to make the slightest contribution particularly to the rayon industry, since the latter requires bisulphite cellulose, whereas from the pines indicated above the cellulose has hitherto been produced exclusively by the soda method or by the sulphate method, being obtained with characteristics that do not satisfy the requirements of the rayon industry.

Nevertheless, from a systematic series of experiments which have led to the present invention, it has clearly emerged that the difficulties hitherto encountered in boiling resinous pines in the bisulphite process are not to be attributed to a different nature of the lignine, but to circumstances that have apparently nothing to do with the suitability of the bisulphite lye for decrusting their cellulose fibres.

Moreover the presence in the woods of the various species of pines of a quantity of resin noticeably greater than in the woods of the firs is not the sole reason for the difficulties hitherto encountered in boiling the woods of the pines with bisulphite. Evidently this accentuates a difficulty which is also present even in some broad-leafed woods, namely the difficulty constituted by the great compactness or solidity of the ligneous tissue. But in addition to this when the percentage of resin in the coniferous woods exceeds a certain limit, the cellulose, which can best be extracted from them by the bisulphite process, gives rise, during the subsequent working thereof, to notable discharges, to such an extent that in the case of pines the industry has ended by completely abandoning all bisulphite boiling. Starting from these considerations the experiments that have led to the present invention have had a triple purpose in view:

(1) The preliminary elimination of a large part of the resin by means of a weak alkaline treatment of the wood, preceding the bisulphite boiling;

(2) The impregnation of the wood thus treated, with a bisulphite lye which is capable, by its penetrating power, of completely impregnating the ligneous tissue, and which is also capable, by its composition, of decrusting the lignified cellulose fibres, even at relatively low temperatures, for instance at temperatures below 110° C.;

(3) The diminishing of the percentage of resin in the cellulose by means of a weak alkaline treatment, which is applied thereto before preparing it in sheets.

The physical and chemical characteristics of the products obtained according to the invention from the woods of various species of resinous pines (*pinus pinaster Sol., pinus pinea L., pinus nigra* Arn., with its sub-species *pinus silvestris L., pinus insignis Dougl., pinus strobus L.*, and the like) show in a tangible manner that the object in view has been fully attained as soon as the products themselves by their title of alpha-cellulose (90 to 93 per cent.), by their resin content (from 0.2 to 0.4%) and by their ash content (from 0.15 to 0.20%), by their copper number (less than 2), by the high grade of bleaching, and by the viscosity being somewhat greater than the ordinary values, perfectly fulfill all the most rigorous demands of the artificial textile industry. Therefore while the process described below justly claims the prerogative of boiling, with a lye having a basis of calcium bisulphite and of sulphurous acid, the resinous woods hitherto regarded as being incapable of being treated by the normal bisulphite process, the same remains typically marked by the above-mentioned characteristics, which, extending to new species of conifers the application of bisulphite boiling, will from this time forth provide a use to a higher degree of extensive pine forests, and will supply, chiefly the rayon industry, with a new and copious source of cellulose of the best quality.

It should moreover be expressly remarked that the process according to the invention, although being particularly worked out for the treatment of resinous pines, is applicable in a most general manner to the boiling of the most varied cellulosic materials, having regard to the fact that the perfect impregnation of the latter with the bisulphite lye, and the particular composition of this lye, render possible the decrusting of the lignified cellulose fibres even at temperatures below 110° C., with the advantage of appreciable saving of sulphur and fuel. In the case of non-resinous

woods, the alkaline treatment interposed between the two bleaching operations may be executed at a lower temperature, for instance between 50 and 60° C., and with a liquor containing 0.2 per cent. of sodium carbonate.

The industrial application of the new process does not present any difficulty in practice, since any installation for bisulphite boiling is capable of applying the process without any change having to be made in its normal equipment. This applies not merely to the digesters, the maximum working pressure of which will likewise be from 6 to 7 atmospheres, but also to the preliminary preparation of the wood, and to the manufacture of the bisulphite lye, as well as to all the mechanical and chemical operations subsequent to the boiling.

Before introducing the bisulphite liquor into the boiler charged with wood, the latter is subjected to a preliminary treatment in the open boiler, at temperatures of from 90 to 95° C. and for a duration of from 1 to 2 hours, with an alkaline liquor containing from 0.1 to 0.2 per cent. of sodium hydrate, employed as usual in the preparation of from 4 to 5 volumes to 1 p. by weight of wood. The alkaline lye having been discharged, and a summary washing having been given to the wood in the boiler itself, the bisulphite liquor is introduced, after previously having been adjusted in its composition in such a manner that after mixing with the water absorbed by the wood, there finally results a liquor containing from 0.5 to 1 per cent. of calcium oxide and from 5 to 6 per cent. of sulphurous anhydride, free and semi-free. The boiling is then initiated by heating indirectly with steam to a temperature of from 106 to 108° C., and this temperature is then maintained constant for the whole duration of the boiling, while the pressure also remains constant at from 6 to 7 atmospheres, assuming that in the course of the boiling there does not occur at any time the slightest leakage of sulphurous anhydride.

At the end of this boiling the pressure is discharged by the known methods, which involve the recovery of the sulphurous anhydride, and the coarse product is washed several times in the boiler itself with hot water, and is then subjected to the customary mechanical treatments, which reduce it to a paste ready for bleaching.

The degree of decrustation which is attained in the boiling described above, when a suitable duration, which varies from 12 to 20 hours according to the wood treated, is given to the latter, is such that the crude product can be bleached by employing moderate quantities of chlorine, amounting to no more than from 4 to 5 per cent. of the bleached product. It is however not necessary to have recourse, before the bleaching, to chlorination with gaseous chlorine or with chlorine water, but the crude product may be treated directly with the bleaching liquor having a base of hypo-chlorites. A lye which has been found particularly active in every case is one which, without being acidified by strong mineral acids, contains about one half of hypochlorous acid in a free state, and the remaining half as a calcium or sodium salt. Within 5 to 6 hours, even at an ordinary temperature, the bleaching is almost complete. The cellulose is then washed abundantly with water, after which to the mass circulating in the vat is added sufficient sodium hydrate to form a liquor containing from 0.2 to 0.3 per cent. thereof. The temperature of the mass is carried to about 90° C., and the mass is caused to circulate for 1 or 2 hours, after which it is thoroughly washed, and finally subjected to a fresh bleaching of short duration, for instance 1 to 2 hours, with a bleaching liquor of the same composition as has been indicated above. It is again washed, and the last traces of hypo-chlorous acid are decomposed with a solution of sulphurous anhydride, which likewise has the effect of diminishing the percentage of ash. After a fresh thorough washing the cellulose is finally ready to be prepared in sheets.

FRANCESCO CARLO PALAZZO.