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PROCESS OF REMOVING COLORING MATTER FROM WOOD PULP

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This invention relates to the removal of coloring matter from wood pulp and it is particularly directed to the actual removal from wood pulp of those materials which are responsible for or cause undesired colors in the pulp or the products produced therefrom.

Ordinary wood pulps, bleached or unbleached, contain materials of varying character, such as waxes, resins, fats, pigments, lignin residues, etc., and these constitute impurities which are more or less colored. While the actual percentages of such impurities present may be very small they are able to produce or cause undesirable effects altogether out of proportion to the percentages of the materials present in the pulp. Such materials are largely responsible for the so-called "pitch troubles" in the paper mill and they confer a dark color to rayon, films, cellulose derivatives and like materials manufactured from the pulp. Perhaps the problem created by these impurities is best illustrated by the fact that their presence prevents the use of otherwise suitable pulp as a raw material for the manufacture of cellulose derivatives, as a filler in the plastics industry, or for conversion into papers of high color stability such as high grade wallpapers and the like.

A preferred method of determining the amount of such coloring matter in a pulp is provided by molding the pulp with a colorless resin and comparing the same colorimetrically with a standard similarly prepared by molding purified cotton linters or a wood pulp completely free from coloring matter. Pulps which appear perfectly white to the eye and which yield no material when extracted with organic solvents frequently display undesired color when so molded.

Impurities very similar to these are found in cotton and in the purification of the latter alkaline solutions have been employed for dissolving or dispersing the impurities under heated conditions. It is also known that the addition of emulsifying agents such as soaps, Turkey red oil and the like substantially enhances the dispersing power of the alkaline reagents. This principle of purification has been adopted as a step in the standard procedure for preparation of chemically pure cellulose for scientific investigations.

Application of such a method of purification to wood pulp has heretofore not been commercially possible, since proposals heretofore made require a high percentage, say 3%, of soap calculated on fibre weight together with substantial amounts of caustic soda applied at temperatures of about 100° C. and for a period of say, four to six hours. With lesser amounts of reagents correspondingly less of the impurities are removed. Soap is relatively expensive and its cost, apart from that of caustic and heat, makes the known application of this method to wood pulp impracticable from a commercial point of view.

The chief object of the present invention is thus to provide a method whereby these impurities may be economically and efficiently removed from wood pulp in commercial practice with a view to making such pulp available for further uses as previously indicated.

In accordance with the invention the pulp at low density is impregnated with an emulsifier in solution containing an excess of caustic soda or the like, then concentrated to high density, in which condition it is maintained at elevated temperature for completion of the reaction, and then thoroughly washed. The method is preferably carried out in a continuous or cyclic manner in which the impregnation liquor is recovered, strengthened as required, and reused for impregnating further quantities of pulp.

Suitable emulsifiers are those which dissolve to practically clear solutions in dilute caustic soda at ordinary temperatures, say up to 25° C. Oleic acid, linoleic acid, sulphonated oils, sulphonated fatty alcohols and the like are suitable but economically oleic acid is preferred. Ordinary soaps are not advantageous. They dissolve to clear solutions only in hot water and on cooling coagulation of colloidal masses occurs. This renders the handling of soap solutions in the mill difficult, as pipe lines, storage tanks and the like are not easily kept free from deposits, particularly during shut downs or interruption of the operation. Furthermore, dilute soap solutions are inclined to undergo hydrolytic splitting, precipitating insoluble fatty acid compounds on or within the fibres of the pulp.

The impregnation liquor containing the emulsifier should have an excess of free caustic soda which enhances the dissolving and dispersing power of the emulsifier and maintains an equilibrium in the liquor during its use. Some of this caustic soda disappears owing to the acid character of some of the impurities dissolved from the pulp. Before reusing the liquor caustic soda and emulsifier is added to renew the liquor and compensate for what has been removed in first use. The liquor reaches a state of substantially stable equilibrium after several repeated usages, in which condition it may be used to best advantage. It is not advisable to raise the free caustic soda

content of the used liquor to that of the fresh liquor, but rather to add only so much caustic soda as has been carried away by the pulp. Thus in the successively repeated reuse and renewing of the liquor, there will be removed in each impregnation only so much of the caustic soda as was newly added. It may be noted that the content of coloring matter in the continuously reused liquor reaches a somewhat similar equilibrium. For example, for the first impregnation the liquor may contain 3–50% of sodium oleate and 3–50% of caustic soda calculated on fibre weight, depending upon the character of the pulp to be treated, the density during impregnation and the extent of purification desired. Assuming, for example, that 10% of the liquor is carried away in the pulp, then 0.3–5.0% of sodium oleate and 0.3–5.0% of NaOH should be added before or during reuse of the 90% of the recovered liquor.

In the continuous operation of the process the liquor in circulation is kept well balanced. The pulp under impregnation should have a slightly higher consistency than the pulp concentrated after impregnation, in order to compensate for the volume of solutions added in renewing the liquor. It is apparent that the higher the density to which the pulp is concentrated after impregnation the smaller will be the loss of chemical reagents.

After the impregnated pulp has been concentrated it is subjected to a mild heat treatment, usually by the introduction of steam. Normally a temperature of 35 to 75° C. maintained for one-half to two hours is sufficient to permit the reaction to proceed to the desired point. The conditions will of course vary with the character of the coloring matter remaining in the pulp after impregnation. The pulp is then washed from the liquor thus removing the rest of the coloring matter. The use of warm water, usually available in the mill, reduces the amount of wash water required. In some cases it is preferable to have the wash water slightly alkaline and for this purpose there may be added thereto, for example, not more than 0.5% of NaOH or the like calculated on the weight of the pulp being washed. The wash water should be low in lime, magnesium, and the like and preferably free therefrom.

It is desirable that the lime content of the pulp to be treated be low, particularly if the emulsifying agent used forms, with lime, salts which are insoluble or difficultly soluble or dispersible. Under these conditions the lime content of the pulp is preferably not more than about 0.02%. With such a pulp the impregnating liquor, containing sodium oleate as the emulsifier, withdrawn after impregnation remains practically clear whereas with a relatively high lime bearing pulp it becomes decidedly turbid. Low lime pulps may be readily prepared for example by the method disclosed in copending application Serial Number 735,437, filed July 16, 1934. It should be mentioned that some emulsifiers, such as sulphonated fatty alcohols, form calcium salts which are soluble and when using such emulsifiers the absence of lime in the pulp is not of particular importance.

One manner of carrying out the invention in a continuous manner may be generally described as follows:—The pulp to be purified is brought to a high consistency of say 25 to 30% and conveyed to a mixing box where the impregnating solution, containing the emulsifier and caustic soda or the like, and if necessary water, is mixed with the pulp reducing its consistency to about 3%. The low density pulp then enters a mixing tank where it is kept in agitation to make the impregnation complete and uniform. The size of this mixing tank need not be greater than to provide for a total impregnation time of about 30 minutes. The pulp mixture is conveyed to another thickener where its density is raised to a point slightly lower than the original density before maceration. The waste liquor is returned to the mix box where with added strengthening materials it is ready for reuse. The concentrated pulp passes to a mixer where the desired temperature is obtained by the introduction of steam or otherwise as desired and thence to a container where it remains until the reaction is complete when it is removed from the container and thoroughly washed. Obviously such a system is quite flexible and the method may be carried out in various ways. By means of weirs and the like the addition of chemicals may be easily controlled and the volume of liquor kept in balance.

The following specific examples are given as further illustrative of the operation of the invention.

(1) An unbleached strong sulphite pulp, containing objectionable impurities amounting to 1.4% as indicated by extraction with organic solvents, was impregnated at a density of 3% with a previously used and strengthened liquor containing 5% of neutralized Turkey red oil and 15% of NaOH, both calculated on fibre weight, for five minutes at ordinary temperature and with thorough agitation or mixing. The pulp was concentrated to 25% density, the removed liquor being returned for reuse, and the temperature of the concentrated pulp was brought up to 40° C. by the admission of steam to the mixer, at which temperature the pulp was allowed to remain for 30 minutes. After washing the pulp free from impregnating liquor it was subjected to a conventional two-stage bleach, the second stage being carried out at a pH higher than 8.0. After washing with slight acidification the refined pulp was very white and developed only slight yellow coloration upon molding with a colorless resin. It contained not more than .25% of material extractable by organic solvents. In addition to its improved color other valuable physical properties of the pulp were better owing to the greater ease of bleaching. The pulp was particularly suitable for conversion into wallpapers and the like on account of its high degree of color stability.

(2) A soft sulphite pulp partly bleached containing not more than .02% CaO and about .9% material extractable with organic solvents was impregnated at a density of 1.5% with a previously used strengthened liquor containing 8% sodium oleate and 6% caustic soda calculated on the pulp for fifteen minutes with thorough mixing. The pulp was concentrated on a wet machine into laps of 30% density, the waste liquor being returned for reuse, and the moist laps were brought to a temperature of 65° C. for 30 minutes, then thoroughly washed and bleached at a pH of 8.5. After washing with slight acidification the pulp developed practically no coloration on molding and contained not more than .15% of material extractable with organic solvents. The pulp was well adapted for high grade uses, such as conversion into cellulose derivatives, viscose rayon, color stable papers or as a filler in the plastics industry.

(3) A soft partly bleached wood pulp, pre-

pared from unbleached pulp by chlorination in the presence of sodium chloride and not containing more than .01% CaO and 1.1% of material extractable with organic solvents was impregnated at 1% density with a previously used liquor containing 12% sodium oleate and 60% caustic soda, calculated on fibre weight, for a period of 15 minutes under normal temperature and with thorough mixing. The pulp was concentrated to a density of 30%, containing in this condition .28% of sodium oleate and 1.4% caustic soda which are lost during washing, the removed liquor being returned to the cycle for reuse. The concentrated pulp was heated to 65° C. for 90 minutes and after washing was bleached with a soda bleach liquor at a pH of above 8.5 to complete whiteness. It was then washed, slightly acidified to remove traces of caustic and rewashed. The bleached pulp contained substantially 90% alpha cellulose and its color was stable under the severest light treatment. A molded product prepared from it and a suitable resin, under pressure and heat remains perfectly white. The pulp does not contain more than .05% of material extractable with organic solvents.

It will be observed that pulp produced in accordance with the invention has advantages in addition to its high color stability. It is recognized that the bleaching of pulp to overcome the discoloring effect of impurities tends to impair physical properties of the pulp by lowering the alpha cellulose content and otherwise. By actually removing the impurities much milder bleaching is required and the damage to the fibre is thus reduced. Indeed the last stage of bleaching is not always required with the present method. The cost of bleaching material and expense is greatly reduced.

A pulp of the invention having an alpha cellulose content of say 91% will provide rayon the equivalent of that produced from known pulps having an alpha cellulose content of 94 or 95%. It will produce an unbleached rayon as white as a bleached rayon produced from ordinary pulps now in use. Thus in the production of rayon from this pulp less handling is required and a larger proportion of number one grade material is obtained.

I claim:

1. A method of refining wood pulp which comprises treating the pulp at low density and at ordinary temperature with a liquor containing an emulsifying agent and an alkali, thickening the pulp to high density, retaining the thickened pulp at a raised temperature to dissolve or disperse impurities and washing the pulp.

2. A method as defined in claim 1 wherein the washed pulp is bleached and then washed with slightly acidified water.

3. A method as defined in claim 1 wherein the operations are carried out continuously and the liquor removed upon thickening the pulp is returned for reuse.

4. A method as defined in claim 1 wherein impregnation is effected at a pulp density of .5 to 5%, the pulp is thickened to a density of 15 to 30% and is then maintained at a temperature of 35 to 75° C. for a period of from one-quarter to three hours.

5. A method as defined in claim 1 wherein the pulp is washed with a warm water containing substantially .5% caustic soda calculated on the basis of the fibre weight of the pulp.

6. A method as defined in claim 1 wherein the treating liquor contains an excess of alkali.

7. A continuous method of purifying wood pulp which comprises impregnating the pulp at low density and at ordinary temperature with a liquor containing an emulsifying agent and an excess of caustic soda, thickening the pulp to high density, returning the used liquor for reuse, subjecting the thickened pulp to a temperature not in excess of 75° C. to dissolve and disperse remaining impurities and washing the pulp.

8. A continuous method as defined in claim 7 wherein the used impregnating liquor is strengthened in emulsifying agent and caustic soda for reuse.

9. A method of purifying low lime wood pulp which comprises impregnating the pulp at low density and ordinary temperature with a liquor containing sodium oleate and an excess of caustic soda, thickening the pulp to a density up to 30%, recovering the impregnating liquor, raising the temperature of the thickened pulp to about 65° C. to dissolve and disperse impurities and washing the pulp.

10. A method as defined in claim 7 wherein a pulp containing not more than .02% CaO is treated.

11. A method of refining wood pulp which comprises treating the pulp at low density and at ordinary temperature with a liquor containing an emulsifying agent and an alkali, thickening the pulp to high density, returning the liquor for reuse, retaining the thickened pulp at a raised temperature to dissolve and disperse impurities and washing the pulp.

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