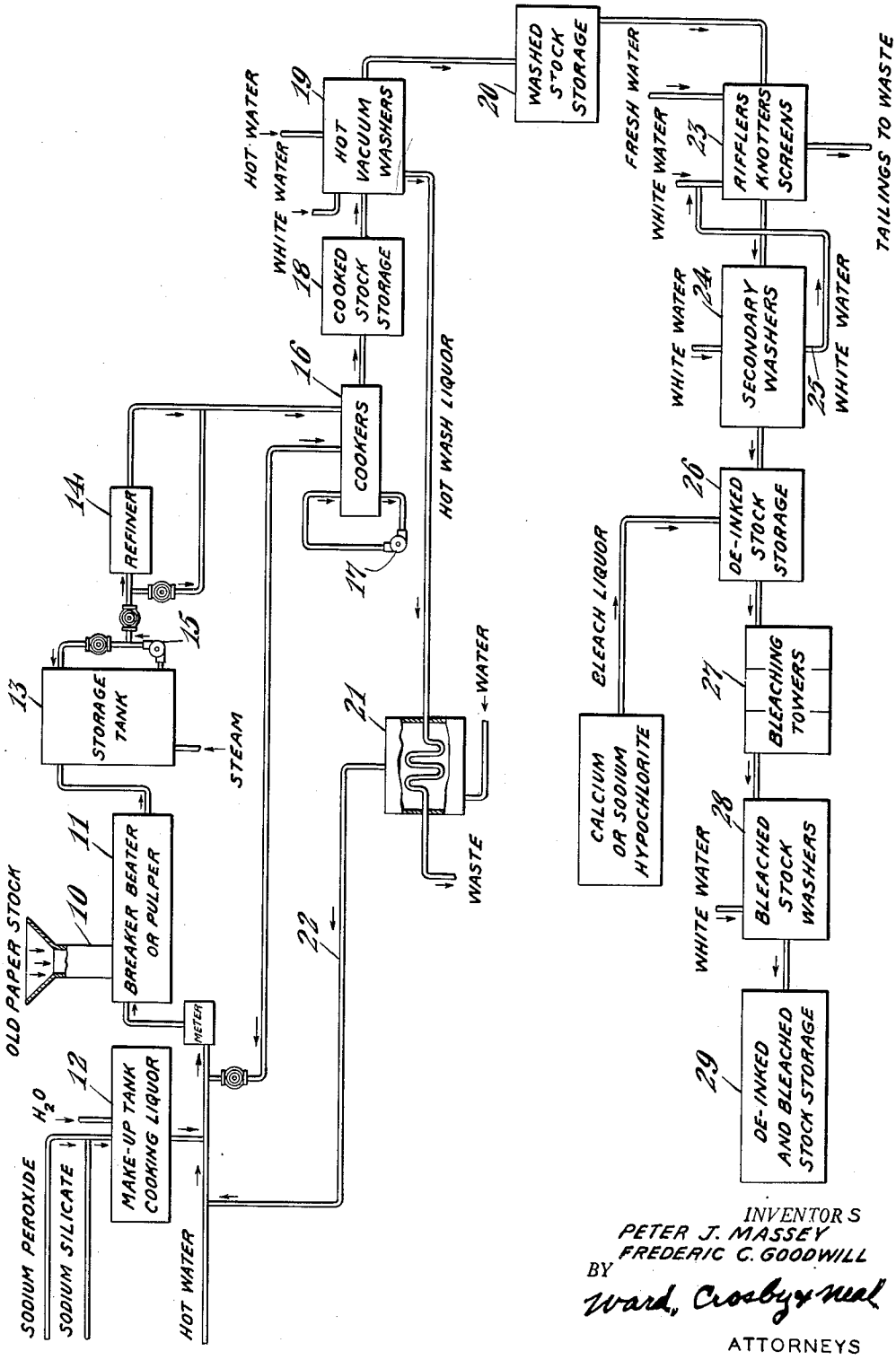
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DEINKING AND BLEACHING OF PAPER

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DEINKING AND BLEACHING OF PAPER

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This invention relates to improvements for de-inking and bleaching printed paper stock such as printed leaflets, magazines, books and the like, the invention being particularly adapted for the de-inking of such stock of types which include a substantial proportion of groundwood.

Heretofore these classes of paper stock were largely formed of chemical fiber "free" of groundwood. However, with the advent of machine coating and the present large demand for lightweight paper to satisfy increased advertising demands, these classes of paper now often include from 30 to 60% of groundwood. As machine-coated and groundwood papers of this class have improved in quality, the percentage of groundwood contained has appreciably increased, with the consequence that the prior conventional methods of de-inking these types of papers by cooking with alkalis such as sodium hydroxide and soda ash, have resulted in depreciating the quality of the resulting finished paper stock in a more or less direct ratio to the increased groundwood content. This is due to the fact that the groundwood portion of the waste paper is attacked by such alkalis, causing the formation of a very brown stock, making this source of waste paper unsuited to the pumping of stock for the manufacture of high brightness white papers.

The present invention relates to a type of de-inking process wherein the paper stock is treated at elevated temperatures in beater or pulper machines and in cookers in the presence of a de-inking solution comprising a peroxide and an alkaline soluble silicate. Thereafter the treated stock is thoroughly washed and then subjected to a bleaching treatment such as by the use of calcium or sodium hypochlorite.

While we are aware that methods have been proposed from time to time over a long period of years for de-inking old paper stock by the use of peroxides and alkaline silicates, yet so far as we are aware, such proposals have not been successful in commercial practice, and even very recent attempts therewith in certain large paper mills have met with failure. Upon extensive experimentation with this type of process in an effort to find the reasons for prior failures, we have determined that various factors involved in the use of solutions such as of sodium peroxide and sodium silicate for de-inking purposes are quite critical. For example, the proportion of alkali to silica in the sodium silicate used appears to be important in that if the proportion of silica is too high, as will be the case if the necessary amount of sodium silicate is used of various

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readily available commercial types, then the treated pulp is so difficult to wash in the presence of excess colloidal silica, that adequate removal of the ink and its binder material is impossible. Other difficulties occur if the proportion of silica is too low as with other commercially available sodium silicates. The amount of the selected sodium silicate to be used also is rather critical and unexpectedly, we have found that the amount used may and should be a very substantially larger percentage of the pulp mixture than is generally the case with de-inking reagents of other types heretofore used. If insufficient silicate is used, the drainage rate of the stock and the consequent possibility of thoroughly washing same to remove the ink particles is made too difficult. On the other hand, if an excess is used, the pulp stock becomes too softened for economical and effective washing.

We have discovered an improved method of de-inking and bleaching, utilizing solutions such as of sodium peroxide and certain sodium silicates, followed by a suitable bleaching treatment, such as will fully overcome the above-noted difficulties and result in a commercially successful practical process for the purpose, in which there is no substantial degradation of the fibers and with which the degree of brightness of the resulting stock is substantially enhanced as compared with all other de-inked stocks made from comparable grades of waste paper, so far as we are aware. The invention makes possible a degree of brightness substantially beyond that attainable heretofore with de-inked pulp stock containing substantial percentages of groundwood.

Various further and more specific objects, features and advantages of the invention will clearly appear from the detailed description given below, taken in connection with the accompanying drawing which forms a part of this specification and illustrates by way of example a preferred arrangement of apparatus or flow sheet for carrying out the invention. The invention consists in such novel methods and combinations of features as may be shown and described in connection with the equipment herein disclosed.

As indicated in the drawing, the old or waste paper stock is introduced through a hopper 10 into a so-called breaker beater or pulper 11, along with a mixture of hot water and the de-inking reagent which, as indicated, may comprise a mixture of sodium peroxide and sodium silicate, which are carefully measured and then introduced and thoroughly mixed together in a

make-up tank 12 for the cooking liquor prior to its introduction to the beater or pulper.

The old paper stock, for example, may comprise paper taken from books, magazines and leaflets, and containing substantial amounts of groundwood, for instance 30 to 60% and upwards. In the beater or pulper the stock is broken down into relatively small pieces and thoroughly wetted and mixed with suitably metered amounts of the cooking liquor solution.

The cooking liquor solution, according to a preferred example, comprises a water solution containing 1½% of sodium peroxide and 6% of sodium silicate, these percentages being by weight as compared with the weight of the dry waste paper to be treated. As an example, 4800 lbs. of sodium silicate and 1200 lbs of sodium peroxide are dissolved in 5000 gallons of water. 125 gallons of such liquor may be used per ton of paper stock.

The form of sodium silicate which we preferably use in one which is commercially available and is in liquid form of a density of about 58.5° Bé. and containing about 19.5% Na_2O and about 31.2% SiO_2. When another example of commercially available liquid sodium silicate was used, viz. one which has a density of about 42° Bé. with about 9.1% Na_2O and 29.3% SiO_2, it was found that the degree of brightness in the de-inked and bleached stock was substantially lower. Other commerciallw available forms of sodium silicate in solid form and which include substantial quantities of the sodium metasilicate proved to be undesirable for the purpose, so far as we could determine, in that the drainage rate of the treated material was so low that the ink particles could not be effectively removed, although in advance it was supposed that this would be the more desirable form of sodium silicate to use as it forms true solutions as compared with the liquid silicates which form colloidal solutions or suspensions. For securing a treated stock with a high degree of brightness, our tests and practice of the invention have indicated that the sodium silicate used should preferably have a molecular ratio of Na_2O to SiO_2 in the neighborhood of 1 to 1.5, since the use of sodium silicates having a lower normal alkaline content, for example for which this ratio was about 1 to 3.2 or more, resulted in the excess production of colloidal silica, interfering with ink particle removal, and on the other hand, the use of forms of sodium silicate having substantially a 1 to 1 ratio of Na_2O and SiO_2 resulted in excessive softening of the pulp with a consequent drainage rate too slow for efficient and economical washing. While for the best results which we have thus far attained, the ratio of Na_2O to SiO_2 was about 1 to 1.3, satisfactory results are believed to be obtainable if this ratio varies within limits of about 1 to 1.4, up to a ratio of about 1 to 2.5, although, with a sacrifice of brightness, a ratio of 1 to 3 or somewhat higher is permissible. A grade of sodium silicate has been found satisfactory, having a specific gravity of 1.68, density 58.5° Bé., 50.7% solids, and containing 19.5% Na_2O and 31.2% SiO^2.

While we prefer, as above stated, to use about 1½% of sodium peroxide and about 6% of the sodium silicate, these percentages may vary for the peroxide from about 0.8% to 3%, and for the sodium silicate from about 4% to 8%. Higher percentages of the peroxide may be used, for example up to 5%, but will ordinarily not prove to be economical, since the improvement in brightness resulting will tend to be too slight to compensate for the added cost. However, the use of excess peroxide will tend to improve the results obtainable with sodium silicate solutions having a higher ratio of Na_2O to SiO_2.

The de-inking solution is preferably introduced with sufficient hot water to give a pulp consistency at the outlet of the beater or pulper of from about 3 to 5%, the hot water being at a temperature such that the mixture in the beater or pulper has a temperature say in the neighborhood of 120° F. or higher. The various portions of the pulp will remain in the pulper or beater only for a short time and until reduced to relatively fine particles, or in case a batch type of beater is used, until substantially all of the particles are reduced to the desired size, for example in a period of about 15 minutes to ½ hour.

The stock as contained in the beater or pulper preferably has a pH of approximately 11, although this may vary within a range of about 10 to 11.5. In lieu of the use of sodium peroxide, the desired action is obtainable from the use of hydrogen peroxide or a mixture of both, with, of course, adjustments of the proportions of alkali and silicate to correspond.

As shown by the flow sheet, the pulp passes from the beater or pulper to a storage tank 13, and then preferably to a "refiner" 14 of one of the available well-known types, for more finely dividing the pulp stock. As indicated, connections may be provided, including a pump 15 for circulating the pulp through the storage tank to cause thorough mixing, especially in case the material has been allowed to stand in the tank. Also connections are provided for passing the pulp either through the refiner or for by-passing this device directly to cookers 16. These are preferably accompanied by suitable connections as shown, including pumps as at 17 for circulating the stock out of and back into the cookers to insure thorough mixing during the cooking operation. The stock is preferably allowed to remain in the cookers for a period of about 3 to 5 hours, at a temperature in the neighborhood of 160°, and at substantially atmospheric pressure, although such temperature may be varied within limits of about 125° to 200° F., depending principally upon the period of cooking. Also some pressure may be used if desired.

From the cookers the stock passes into the cooked stock storage tank 18, and thence preferably, aithough not necessarily, through vacuum washers 19 where the stock is first diluted with white water and then subjected to showers of hot water and to additions of diluting water in sufficient amounts whereby, after the vacuum washing, it will again have a consistency in the neighborhood of 3 to 6%.

The use of the hot vacuum washing treatment immediately after the cooking step serves to dispose of the greater part of the liquid containing the ink and its binder materials before the same have a chance to again penetrate or become attached to the fibers, and makes more effective the later additional washing treatments. This insures that practically all noticeable traces of the ink are removed, so that the final bleaching treatment is more highly effective. The hot vacuum washing step, as indicated by the flow sheet, also makes available a supply of hot water as a source of heat, partially recovered from the cooking step, and with which the hot water originally introduced at the beater may be heated. For this purpose, from the hot vacuum washers the hot waste liquor is drawn off and passed through a heat exchanger as at 21 for heating a source

of water supply **22** to be introduced into the beater or pulper.

From the vacuum washers (if used) the stock is passed into a washed stock storage tank **20** and through suitable cleaning apparatus such as rifflers, knotters and screens at **23** with accompanying additions of fresh water and white water to make up for the tailings passed to waste and to dilute to a consistency suitable for screening, viz. in the neighborhood of 1% for example.

The stock preferably is then passed through secondary washers **24** with accompanying additions of white water sufficient to make up for the white water which may be withdrawn as through connection **25** for supply to the rifflers, knotters and screens etc., and to maintain the treated stock at a consistency of about 1%.

As shown, thereafter the de-inked stock passes into a storage tank **26**, wherein bleach liquid is introduced, for example in the form of calcium or sodium hypochlorite for bleaching the stock in bleaching towers **27**. In these bleaching towers the stock at a consistency of about 3 to 5% is treated for about 1 to 3 hours (preferably 1½ to 2 hours) at a temperature of about 90 to 120° F., (preferably 100 to 105° F.). The bleaching liquor is preferably made as a water solution containing sodium hypochlorite in amounts equaling (when in solid form) about ¾ to 1½% by weight of the pulp to be treated (air dry basis). The percentage of sodium hypochlorite may, however, vary from about ½ to 2%, as feasible practical limits. A typical example of the bleach liquor may be made by dissolving 2250 lbs. of caustic soda and 2000 lbs. of chlorine in 4900 gallons of water. This provides a solution containing 50 grams of available chlorine per liter. 100 gallons of this liquor is used per ton of stock to provide an equivalent of approximately 2% of available chlorine per ton of stock. Other alkali or alkaline earth hypochlorites such as calcium hypochlorite may be used.

After bleaching, the stock is further washed at **28** and passed to a storage tank **29** in the form of de-inked and bleached stock.

It is believed that the action of the peroxide in the above-described process is largely a protective one, inhibiting the normal discoloring action of alkali on cellulose fibers, particularly those of such nature as groundwood fibers. It is not contemplated that the peroxide is to act in this process with a bleaching effect, since the stock, as it leaves the cookers, is not appreciably bleached, but requires a subsequent bleaching for brightening effect. The stock as it leaves the cookers ordinarily has a degree of brightness no greater than the unprinted portions of the stock originally introduced. While the avoidance of discoloring of the stock has been the aim of de-inking processes heretofore, it has not been achieved in the presence of substantial amounts of groundwood in view of the browning and discoloration caused by the alkalis present acting on the groundwood.

The action of the silicate first, is as a so-called wetting agent permitting more rapid and more through wetting of the paper and thereby aiding disintegration. Secondly, it has detergent properties which are very effectively brought into action. The colloidal silicate will collect the ink particles, keeping them separate from the fibers and permitting of more thorough removal during the successive washing steps. By the use of sodium silicates having properties within the limits above recommended, it is possible promptly and thoroughly to wash from the cooked stock substantially all of the ink material, whereas if other types of sodium silicate are used, the difficulties of washing and draining the stock have been, according to our experience, so great as to preclude practical use of such a process.

Experience has also shown that the introduction of de-inking chemicals in the beater rather than at a later stage, such as in the cookers, is much more advantageous, since the time during which the chemicals are in contact with the pulp is lengthened and the chemicals are promptly brought at full strength into more intimate contact with the fibers, and at a temperature much lower than in the cookers, thus providing a longer time for the chemicals to act before their effectiveness becomes spent at the higher cooking temperature. However, the de-inking chemicals should not be allowed to stand in contact with the pulp for any prolonged period before the mixture is cooked and washed, because in that event there may be an appreciable degradation in color of the finished stock.

With the above process, it has been found that while the degree of inherent brightness of the fibers of the groundwood stock is not improved by the de-inking steps, yet upon then subjecting to the bleaching step with calcium or sodium hypochlorite, the stock brightness is increased to an unexpected degree, and to about 60 to 65 as measured by the General Electric reflectance meter, or so-called standard brightness testers. That is, with the stock as de-inked by this process, and despite the large content of groundwood, the hypochlorite bleaching treatment may be used with greater efficiency than on other types of groundwood stock. No comparable brightness, so far as we are aware, has heretofore been achieved with de-inked pulp stock containing substantial amounts of groundwood, such as from 30 to 60%. By especially careful treatment, the brightness may be even further increased up to about 70.

While the invention has been described in detail with respect to particular preferred examples, it will be understood by those skilled in the art after understanding the invention, that various changes and further modifications may be made without departing from the spirit and scope of the invention, and it is intended therefore in the appended claims to cover all such changes and modifications.

What is claimed as new and desired to be secured by Letters Patent is:

1. A process for removing printer's ink from printed paper stock to form a pulp for reuse in paper making, which comprises: subjecting such stock to a pulping treatment in hot, aqueous, de-inking medium such as to produce a pulp consistency of about 3 to 5%, said medium containing as de-inking reagents about 0.8 to 5% of sodium peroxide and about 4 to 8% of sodium silicate having a molecular ratio of sodium oxide to silica within limits of about 1:1.4 to 1:3, said reagent percentages being by weight of the dry paper weight, cooking the resulting mixture at a temperature of about 125° to 200° F. for about 3 to 5 hours, and thereupon washing said resulting pulp to free the same of said link and de-inking medium.

2. A process for removing printer's ink from printed paper stock to form a pulp for reuse in paper making, which comprises: subjecting said stock to a pulping treatment in hot, aqueous, de-inking medium, such as to produce a pulp

consistency of about 3 to 5%, said medium containing as de-inking reagents about 1 to 1.5% of sodium peroxide and about 6% of sodium silicate having a molecular ratio of sodium oxide to silica within limits of about 1:1.4 to 1:2.5, said reagent percentages being by weight of the dry paper weight, cooking the resulting mixture at a temperature of about 125° to 200° F. for about 3 to 5 hours, and thereupon washing the resulting pulp to free the same of said ink and de-inking medium.

3. A process for removing printer's ink from printed paper stock to form a pulp for reuse in paper making, which comprises: subjecting said stock to a pulping treatment in hot, aqueous, de-inking medium, at a temperature upwards of 120° F. and in proportion such as to produce a pulp consistency of about 3 to 5%, said medium containing as de-inking reagents about 1 to 1.5% of sodium peroxide and about 6% of sodium silicate having a density of about 1.7 and a molecular ratio of sodium oxide to silica within limits of 1:1.4 to 1:2.5, said reagent percentages being by weight of the dry paper weight, cooking the resulting mixture at a temperature of about 125° to 200° F. for about 3 to 5 hours, and then, while hot, vacuum washing the resulting pulp, to eliminate said de-inking medium and the ink therefrom.

4. A process for removing printer's ink from printed paper stock to form a pulp for reuse in paper making, which comprises: subjecting said stock to a pulping treatment in hot, aqueous, de-inking medium such as to produce a pulp consistency of about 3 to 5%, said medium containing as de-inking reagents, a peroxide oxidizing agent equivalent to about 0.8 to 5% of sodium peroxide, and an alkali metal silicate equivalent to about 4 to 8% of sodium silicate, having a molecular ratio of sodium oxide to silica within limits of about 1:1.4 to 1:3, said reagent percentages being by weight of the dry paper weight, cooking the resulting mixture at a temperature of about 125° to 200° F. for about 3 to 5 hours, thereupon washing the resulting pulp to free the same of said de-inking medium and the ink material, and thereupon subjecting said pulp to a bleaching treatment.

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