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(54) **Manufacture of pulp.**

(57) Processes for producing pulp from lignocellulosic material in which the delignification agent comprises an alkali metal hydroxide together with a small amount of a sulphite in the range between 0.1 and 15% expressed as Na_2SO_3 by mass on an oven dry basis of said lignocellulose. The addition of the small amount of sulphite gives a marked improvement in both the quality of the paper produced from the pulp and the rate of delignification. The rate of delignification is improved further by the use of a redox agent such as anthraquinone, anthrahydroquinone, homologues and derivatives thereof. Optionally, the process may be carried out in two stages, including a first stage in which lignocellulose is digested in a liquor containing between 0.1 and 15% of a sulphite, and another further stage in which said lignocellulose is digested in a liquor containing an alkali metal hydroxide.

The pulping liquors may also contain other alkaline compounds such as sodium carbonate which act as buffers.

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Description

Manufacture of Pulp

This invention relates to pulp and paper manufacture and has been devised particularly although not solely to provide methods of manufacture of high strength lignocellulosic pulps, and the lignocellulosic pulps manufactured thereby.

In known chemical or semi-chemical pulping of lignocellulosic materials such as wood an objective is to selectively dissolve or soften the lignin component therein in order to release the fibrous cellulosic component with the minimum of attack thereof. The lignocellulosic materials are digested by contact with a pulping liquor at elevated temperature for a substantially predetermined time.

The pulping liquors used in lignocellulosic pumping may be conveniently grouped in accordance with the main chemical process by which delignification is achieved.

One group of pulping liquors essentially require the presence of an alkali as the principal deignifying agent, being usually one or more of the alkali metal hydroxides, of which sodium hydroxide is the common alkali used. The use of this group of pulping liquors relies upon selective attack of the lignin component of the lignocellulose by alkali to achieve delignification. Processes using this group of pulping liquors are known in the industry as alkaline pumping.

To a much lesser extent some of the alkaline earth metals such as calcium for example, have been used in pulping liquors which may loosely fall into this group, but sodium hydroxide is the common caustic used.

Another group of pulping liquors essentially require the presence of sulphur in the form of a sulphite or bisulphite as the principal delignifying agent, sodium sulphite or sodium bisulphite being the most common compounds used. The use of this group of pulping liquors relies upon sulphonation of the lignin component of the lignocellulose by the sulphite or bisulphite as the fundamental reaction to achieve delignification. This delignification may be conducted under either acidic or basic conditions, sodium bisulphite being the common sulphite used for acidic sulphonation and sodium sulphite for basic sulphonation.

Discoveries that hot aqueous alkali liquors are capable of selectively degrading and dissolving lignin, thus allowing the separation of cellulosic fibres from lignocellulosic vegetable tissues were made in England in the nineteenth century, but it was not until 1851 that Burgess and Watt developed the method known today as the soda process which uses a pulping liquor containing sodium hydroxide in the alkaline pulping of wood. The present invention is particularly related to the soda process.

From the original process for alkaline pulp production, the soda process, the kraft or sulphate process developed. Although the first patents on the use of sulphides in the pulping of wood are those of Eaton in the United States of America, in 1870 and 1871, C.F. Dahl of Danzig in Germany is usually credited with the development of the kraft or sulphate process in 1879 when he began to substitute sodium sulphate for the more expensive sodium carbonate used to replace the alkali lost in the process of pulping and chemical recovery. Sodium sulphate is itself inactive in alkaline pulping but in the recovery furnace is reduced to sodium sulphide which in the presence of the caustic liquor, significantly modifies the delignification process.

The kraft or sulphate process has advantages (when compared with the soda process) of producing pulps of increased strength and yield and at increased rates of delignification but the high levels of sulphur contained in the pulping liquor continue to be of concern from the viewpoint of nuisance and pollution. There remained therefore, an interest in the soda process in spite of the inferior pulp quality and slower delignification rate which results, mainly because it offers advantages of less pollution and a simpler chemical recovery system.

It has been recognised for many years that the alkali, in addition to attacking the lignin component, also but to a lesser extent, attacks the carbohydrate molecules which make up the cellulosic fibres, and it was anticipated that any improvement in selectivity of delignification would result in a yield increase and/or an improvement in pulp strength properties.

It was then demonstrated that in alkaline pulping, the compounds borohydride and hydrazine inhibited degradation of the carbohydrate to protect the cellulosic fibres and thus improve the selectivityof delignification. Both borohydride and hydrazine can provide increased yields but they are unstable in the conditions existing in the alkaline pulping process. Relatively large addition levels are therefore required to be effective, since thse compounds are themselves destroyed during the process and the protection which they provide is lost. The cost of these compounds and the large addition levels required, make their commercial use uneconomic.

However, encouraged by these results and results obtained with redox agents, work continued with the goal being to modify the alkaline wood pulping process through the use of redox agents as stable to alkali as possible. The following publication appeared in the Abstract Bulletin of the Institute of Paper Chemistry (Volume 43 No 6), December, 1972.

"6197 (T). Bach, B.; Fiehn, G.

NEW POSSIBILITIES FOR CARBOHYDRATE STABILIZATION IN ALKALINE PULPING OF WOOD.

Zellstoff Papier 21, no. 1:3-7 (Jan., 1972).

(Original in Gar.; Engl transl. available from IPC on share-the-cost basis).

Studies of 25 agents (selected on a redox-potential basis) with respect to their carbohydrate stabilization capacity during alk. pulping (testing was actually conducted on hydrocellulose being trd. in 2 N caustic soda soln.) showed both hydroxylamina and anthraquinone sulfonates to have substantial stabilizing capacities,

while that of hydrazine was surprising light. Further studies comparing the stabilization capacities of hydroxylamine and 2-Na-anthraquinonemonosulfonate as a function of concn. revealed a superior capacity for the latter cpd. Expts. involving anthraquinone sulfonate addns. in sulfate and soda pulping showed that with increasing addn. (up to 5 and 3% resp.) pulp yields increased (in the case of sulfate pulping, from less than 44% up to over 51%) while rejects decreased to less than 1%. Selectivity of delignificaion was also markedly improved. The resulting pulps were brighter with higher stretch and breaking length, but reduced tearing strength. The reaction mechanism of the anthraquinone derivatives in alk. pulping is not yet clear, but a parallel appears to exist to polysulfide pulping. Due to the stability of the anthraquinona structure at high temps. in alk. medium, the stabilizing effect occurs over the total alk. cooking cycle, accounting for the high efficacy of this pulping additive. 21 ref. L.G.S."

The publication is based on the results of German workers B. Bach and G. Fiehn who selected agents for addition to alkaline pulping processes ona redox-potential basis. In working out the experimental procedures they took the following factors into account:

1. "The anthraquinone structure is, as is well known from dye chemistry, stable inalkaline medium even at elevated temperatures. Therefore, one can expect that the stabilizing action of anthraquinone derivatives is present not only at the beginning of the wood pulping process, but, in contrast to other known wood pulping additives, throughout the entire cook. This means that marked effects can be expected already at slight additions."
2. "Anthrquinone derivatives are the starting point in the synthesis of commercial cotton dyes. Therefore, the possibility should exist for obtaining commercial grade anthraquinone derivatives in commercial quantities."

It was discovered that athe anthraquinone structure was stable in the environment of th alkaline pulping liquor and was effective in increasing yield by protecting the carbohydrate to some extent from attck by the pulping liquor alkali, while at the same time accelerating the delignification reactions.

Since the common alkali used is sodium hydroxide the process became known as "Soda/Anthraquinone" of Soda/AQ pulping. The name Soda/AQ pulping is applied by the pulp and paper industry to processes when the principal delignifying agent is sodium hydroxide andwhere the additive is an anthraquinone, including anthraquinone per se and derivatives of anthraquinone.

The Soda/AQ pulping process results in a pulp product which compares favourably with the kraft process in all respects except that the tear strength of paper resulting therefrom, is significantly inferior.

A further major discovery was made in 1976 when the Australian workers Farrington, Nelson and Vanderhoek found that anthraquinone and anthrahydroquinone type compounds were active in favourably influencing delignification using sodium sulphite. Sodium sulphite belongs to the second group of pulping liquors described hereinbefore where the chemistry of delignification is quite different to that of the first, and it was therefore surprising to again find the benefits of increased yield and increased rate of delignification.

The discovery is used in the NS/AQ (neutral sulphite/anthraquinone) process where sodium sulphite is the delignification compound and in the AS/AQ (alkaline sulphite/anthraquinone) process where sodium sulphite and sodium hydroxide are both used together in large amounts as joint delignification compounds.

Of these two processes the AS/AQ process produces pulp which approaches that of kraft, but at the very least has a relatively unproven liquor regeneration system although the pulping rate is similar to kraft pulping. The NS/AQ process has a slower pulping rate and is therefore recognised as more suited to semi-chemical pulping, (often called the NSSC/AQ process), where a lesser degree of delignification is used, and higher pulp yields are obtained. There is no suggestion that NS/AQ pulp is any match for kraft of course; it has a substantially lower tear for example.

The kraft process is renowned for the strength of the packaging paper produced from the pulp, which is also used as a reinforced fibre in other papers such as newsprint, printing and writing papers for example.

The soda process is renowned for simplicity of chemical recovery and a relatively low level of environmental pollution, but as B. Bach and G. Fiehn found, Soda/AQ pulping produces pulp incapable of matching the tear strength of kraft pulp when manufactured into paper products. The inferior tear strength of Soda/AQ pulps has been confirmed by many workers since.

There is therefore a need for a method of manufacture of high strength lignocellulosic pulp which retains the relative simplicity and low level of environmental pollution of the Soda/AQ process while at the same time producing pulp which matches kraft pulp in strength.

It is therefore an object of this invention to provide methods of manufacture of high strength lignocellulosic pulps and the lignocellulosic pulps manufactured thereby.

It is also an object of this invention to provide a useful alternative pulping liquor system for the delignification of lignocellulosic materials.

Other objects of this invention will become apparent from the following description.

According to one aspect of the invention there is provided a pulping liquor for use in the digestion of lignocellulose, in the manufacture of lignocellulosic pulp, including an alkali metal hydroxide delignification agent and a sulphite, said sulphite being present in amounts of between 0.1% and 15% expressed as Na_2SO_3 by mass on oven dry mass of said lignocellulose.

According to a further aspect of the invention there is provided a pulping liquor for use in the digestion of lignocellulose, in the manufacture of lignocellulosic pulp, including an alkali metal hydroxide delignification agent and a sulphite, said sulphite being present in amounts of between 0.1% and 10% expressed as Na_2SO_3

by mass on oven dry mass of said lignocellulose.

According to a further aspect of this invention there is provided a method for use in the manufacture of lignocellulosic pulp, including digesting lignocellulose in contact with an aqueous pulping liquor containing alkali metal hydroxide as a principle delignifying agent, in the presence of a redox agent selected from anthraquinones and anthrahydroquinones and/or derivatives thereof, and a sulphite, said sulphite being present in amounts of between 0.1% and 15% expressed as Na_2SO_3 by mass on oven dry mass of said lignocellulose.

According to a further aspect of this invention there is provided a method of use in the manufacture of lignocellulosic pulp, including digesting lignocellulose in contact with an aqueous pulping liquor containing alkali metal hydroxide as a principle delignifying agent, in the presence of a redox agent selected from anthraquinones and anthrahydroquinones and/or derivatives thereof, and a sulphite, said sulphite being present in amounts of between 0.1% and 10% exprssed as Na_2SO_3 by mass on oven dry mass of said lignocellulose.

According to a further aspect of this invention there is provided a method for use in the manufacture of lignocellulosic pulp, including one stage in which lignocellulose is digested in a liquor containing between 0.1% and 15% of a sulphite and another further stage in which said lignocellulose is digested in a liquor containing an alkali metal hydroxide as a delignification agent, said sulphite being expressed as a percent Na_2SO_3 by mass on oven dry mass of said lignocellulose.

According to a further aspect of this invention there is provided a method for use in the manufacture of lignocellulosic pulp, including one stage in which lignocellulose is digested in a liquor containing between 0.1% and 15% of a sulphite and another further stage in which said lignocellulose is digested in a liquor containing an alkali metal hydroxide as a delignification agent, said sulphite being expressed as a percent Na_2SO_3 by mass on oven dry mass of said lignocellulose; liquor in at least one of said stages including a redox agent selected from anthraquinones, anthrahydroquinones and/or derivatives thereof.

This invention, which includes the foregoing will now be described by way of example with reference to the following drawings, wherein:

Figure 1: which shows a tear index over a range of sheet densities for a kraft pulp and a Soda/AQ pulp prepared under similar pulping conditions.

Figure 2: which shows a comparison of the strengths of four pulps, being conventional kraft and Soda/AQ pulps together with two pulps manufactured by the sulphite pre-treatment two stage method and the sulphite single stage method of this invention, the comparison being made by plotting Tear versus Burst.

Figure 3: which shows a comparison of Tear index for kraft, Soda/AQ and pulps manufactured in accordance with the methods of the invention both before and after bleaching.

Figure 4: which shows an inter-relationship between the amount of alkali metal hydroxide delignification agent and sulphite used in the pulping liquor, the H Factor used for the digestion and the pulp Kappa number resulting therefrom.

Throughout the specification, reference is made to a redox agent. It should be appreciated that any appropriate redox agent can be used, although there are advantages to be gained from the redox agent being selected from anthraquinone, anthrahydroquinones and/or derivatives thereof. In one form of the invention, and for the purposes of this invention preferred redox agents may be defined as being selected from anthraquinones, anthrahydroquinones and/or derivatives thereof, including those which contain the anthraquinone structure, including anthraquinones, anthrahydroquinones, their homologues, and/or derivatives, including alkyl, alkoxy, hydroxy, amino, halo, sulphonate, or carboxy derivatives and including also anthraquinone, anthrahydroquinone, anthroquinonemonosulphonate, tetrahydroanthraquinone, sodium or potassium salts thereof, and tautomeric forms of any of these compounds.

By the present invention, we have discovered that lignocellulosic pulp, comparable to Kraft pulp, may be prepared by the digestion of lignocellulose, such as wood, in contact with an aqueous pulping liquor, containing an alkali metal hydroxide and which includes a predetermined or desired amount of sulphite. In the preferred form of the invention, the sulphite is present in the liquor in an amount of between 0.1% to 15%, expressed as Na_2SO_3 by mass on the oven dry mass of the lignocellulose. In some forms of the invention however, the amount can be present from between 0.1% and 10%.

It has been found that amounts (preferably relatively small) of sulphite enhance the strength of the pulps and overcome or minimise the inferior tear strength of the resultant product, (when compared for example with conventional Kraft products).

In a preferred form of the invention, the pulping liquor includes an alkali metal hydroxide as the principal delignification agent and one or more redox agents, such as for example selected from anthraquinones and anthrahydroquinones and derivatives thereof.

It has however been found that the pulping liquor including an alkali metal hydroxide, and including a predetermined or desired amount of sulphite, provides a substantially improved product and acts to overcome or minimise the inferior tear strength, which usually results from manufacture by for example known Soda/AQ processes.

We have also discovered that in one variation of the invention the sulphite component may be included in a liquor used as a pre-treatment to the lignocellulose prior to digestion with alkali metal hydroxide so that two separate liquors may be used for example, to facilitate chemical recovery. In a preferred form of this

embodiment of the invention, at least one of said liquors also contains a redox agent which may be a preferred redox agent such as anthraquinone and anthrahydroquinone and derivatives thereof.

It will become apparent to those skilled in the art that further variations are possible within the scope and spirit of the invention wherein relatively small amounts of sulphite are used, if desired in association with redox agents selected from anthraquinones and anthrahydroquinones and/or derivatives thereof to effect delignification by processes including alkali metal hydroxide as a principal delignification agent.

The main processes to which the invention may be applied include chemical pulping processes of either the liquid or vapor phase types, with or without pre-treatment of the lignocellulose.

Other processes to which the invention may be applied are those where lignocellulose is delignified to a greater or lesser degree prior to mechanical attrition with or without additional heat and/or pressure, including for example, various semi-chemical, chemi-mechanical and chemi-thermomechanical pulping processes.

The invention is particularly suited to chemical pulping processes of either the liquid phase or vapor phase type as an alternative to the kraft process, and in a preferred form may broadly be described as an improvement on the Soda/AQ process, the improvement being due to the presence of a sulphite additive as well as a redox agent additives selected from anthraquinones and anthrahydroquinones and derivatives thereof to improve the selectivity of delignification and enhance pulp strength.

Preferred sulphite additives are the alkali metal sulphites and of these a more preferred sulphite is sodium sulphite, Na_2SO_3.

The principal delignification agent is an alkali metal hydroxide, being a hydroxide of lithium, potassium or sodium used either separately or in combination, the preferred hydroxide being sodium hydroxide. It should be appreciated however, that other delignifying agents can be used if desired.

Although sodium hydroxide is preferred as a principal delignifying agent, the pulping liquor may also contain weaker alkali such as carbonates of the alkali metals, lithium, potassium or sodium, and also hydroxides of the alkaline earth metals magnesium or calcium, these weaker alkalis being useful as buffering agents for example.

Redox agents used in the present invention are preferably selected from anthraquinones, anthrahydroquinones and derivatives of any of these compounds. Other redox agents can be used if desired however.

Examples only of suitable redox agents are anthraquinone, anthrahydroquinone, and sodium or potassium salts of anthraquinone or anthrahydroquinone derivatives such as anthraquinonemonosulphonate and tetrahydroanthraquinone for example. Anthraquinone and sodium tetrahydroanthraquinone are preferred redox agents, but other derivatives and tautomeric forms may be used.

The present invention may be employed in the production of pulps from a range of plant lignocellulose sources, but will be described herein with reference to the pulping of wood, particularly softwood chips, and by way of example only, the pulping of Pinus radiata wood chips. The present invention may be employed in the production of pulps from other wood species however, including both softwood and hardwood species.

Although the Soda/AQ process is now well proven technology and undoubtedly one of the most promising alternatives to the kraft process for producing chemical pulp, a major factor limiting its commercialisation is that the pulps produced by this process are not as strong as their kraft equivalents. This we believe is due to attack on the carbohydrate component of the fibre. In the process of the present invention the alkali metal hydroxide remains the principal delignifying agent with the sulphite being added primarily to stabilise the carbohydrate component of the fibre in addition to the stabilising/delignifying function already provided by the redox agent such as an anthraquinone type compound.

To evaluate the efficacy of the present invention three separate samples of Pinus radiata wood chips were obtained and experimental pulps were manufactured in accordance with normal kraft and Soda/AQ pulping methods as well as both the two stage pre-treatment method and the single stage method of the present invention.

Every effort was made to prepare pulps as similar as possible so that a direct comparison could be made between them.

The three chips samples were found to have the following moisture contents and density:

SAMPLE	DENSITY (kg/m^2)	MOISTURE CONTENT (% OD)
1	446	45.6
2	440	43.8
3	485	47.6

All the chips were screened and those passing through a 22 mm screen and retained on 19 mm, 16 mm and 13 mm screens were combined to provide a uniform supply for use in the study.

The pulps manufactured for the bleaching study were prepared in a 10 litre Weverk rotary digester using 1000 grams (oven dry) of chips. All other pulping was done in a six unit Stalsvats rotary digester using 200 grams (oven dry) of chips in each bomb. The liquor to wood ratio was 2.5 : 1 for the pretreatments and 4 : 1 for the kraft and Soda/AQ digestions. All of the bombs (vessels) were evacuated and flushed with nitrogen prior

to the digestions.

High yield pulps were defibred in a laboratory Bauer disc refiner prior to Kappa number determination. Low lignin pulps were defibred with a propeller stirrer operating at 1425 rev/min for 10 minutes and then passed through a 0.25 mm slotted Packer screen and the total and screened yields determined. Kappa numbers of the screened pulps were determined by a half-scale modification of Appita standard method P201 m-59. The handsheet properties were determined after beating for 2,000, 4,000, 8,000 and 16,000 revolutions in a PF1 mill at 10% consistency with an applied load of 1.8 kg/cm using standard Appita procedures. Appita is the Technical Association of the Australian and New Zealand Pulp and Paper Industry.

Bleaching using a D_CEDED sequence was done on 120 g (o.d.) pulp samples using polyethylene bags for all bleaching stages. Spent bleaching liquors from the D_C, D_1 and D_2 stages were analysed for residual available chlorine by titrating against 0.1 N $Na_2S_2O_3$. After the D_2 stage the pulp was washed with SO_2. Pulp brightness was measured according to SCAN standard C11 : 75 at 457 mm with a Zeiss "Elrepha" reflectometer. Aged brightness was measured after 1 hours at 105°C.

So far as possible the methods we used to prepare, bleach and evaluate the pulps were selected to simulate normal pulpmill practises, and they are described by way of example only to illustrate the invention as is the use of Pinus radiata wood chips. and not to be limiting in any way.

The invention may for example be used with the normal range of liquor to wood ratios in either vapour phase or liquid phase digestions, using digesters of either continuous or batch types, and both softwood and hardwood species of wood may be processes.

In the first instance, we were able to confirm and illustrate the inferior tear strength of Soda/AQ pulp when compared with kraft. With reference to Figure 1 herein, we found in a comparison of the strength properties of our Soda/AQ and kraft pulps, which had Kappa numbers of 31.1 and 27.0 respectively, the tear strength of the Soda/AQ pulp was significantly lower than the kraft pulp, even though both of these pulps were prepared using the same Effective Alkali and H Factor.

Thus we were able to clearly confirm and to illustrate the comparative deficiency in tear strength of Soda/AQ pulp as first reported by B. Bach and G. Feihn some years ago, and since confirmed many times.

We then evaluated a sulphite pre-treatment prior to Soda AQ pulping, the purpose being that a two stage treatment of this type, if successful in improving strength properties, would at the very least offer the opportunity if desired, to keep the sulphite and soda liquors separate in order to broaden the options for chemical recovery.

In the pre-treatment experiments we included 0.05% of the redox agent anthraquinone (% mass on oven dry wood) and digested the wood chips in the pre-treatment liquor at a top temperature of 175°C. With an H factor of 1560 the resultant yield was 68.4% and the Kappa number was found to be 125.6. The pre-treatment liquor contained 14.0% sodium sulphite (% mass on oven dry wood), and the delignification agent used in the second stage was sodium hydroxide.

The pretreatment liquor composition is not narrowly critical and the abovementioned composition is by way of example only, in order to illustrate the invention, and is not intended to be limiting.

With reference to Figure 2 which shows a comparison of the strengths of four pulps, being conventional Kraft and conventional Soda/AQ pulps, together with two pulps manufactured by the methods of the present invention, plotting Tear versus Burst, the effect of including small amounts of sulphite can be clearly seen.

Whereas the Soda/AQ pulp was previously weaker than the kraft pulp, the two stage sulphite pre-treated pulp now had the same or similar tearing strength to the kraft control. The sulphite pre-treatment had achieved the improvement in tearing strength without reduction in the other strength properties.

It was appreciated that while the pre-treatment method may keep the two liquor systems separate to possible advantage in chemical recovery, the single stage treatment would in most instances be far more preferable in the interests of minimising process costs. For this reason examples of the single stage method of the invention wherein a single digestion is conducted with minor amounts of both a preferred redox agent and a sulphite together with alkali metal hydroxide as the main delignifying agent were also investigated. Surprisingly, even in the presence of the known strong influence of anthraquinone in modifying delignification reactions, the effect of a small amount of sulphite was to increase the selectivity of alkaline delignification, as indicated in Figure 2 by the similarity in pulp strength produced by both the two stage and single stage embodiments of the invention, and particularly the ability of the sulphite to raise the tear strength of the pulps to that of kraft pulp. The invention has been found to eliminate or at least minimise a deficiency in the prior art soda process which has been recognised for many years and even very small amounts of sulphite have been found to provide improvements in selectivity of the soda delignification process.

We refer to Figure 3 which shows a comparison of Tear Index for kraft, Soda/AQ, the pulps manufactured in accordance with the methods of the invention both before and after bleaching. We have investigated the effects of bleaching of pulp made in accordance with the methods of this invention using a conventional D_CEDED 5-stage bleaching system, and as shown in Figure 3, we found that the strength properties of the pulp were retained after bleaching.

Three pulps were prepared by way of example from Pinus radiata chips, these being conventional kraft, Soda/AQ and the pulp of the present invention, all having comparable Kappa numbers between 28 and 30. The brightness range of the pulps after bleaching was in the range 87.1 to 87.7 with the pulp of the present invention being 87.3. The aged brightness of the pulps after bleaching was in the range of 84.9 to 85.8 with the pulp of the present invention being 85.2. The results indicated that all of the pulps required similar bleaching

conditions and that the pulp of the present invention gave a similar bleaching response to that of conventional kraft. The present invention therefore provides a high strength bleachable grade pulp with properties similar to conventional kraft pulp.

Within the limits of precision of our experiments, we have found little difference between pulps prepared with 14.35% sulphite addition and those prepared with 2.71% sulphite addition and those prepared with 8.53% sulphite addition. Below about 4% sulphite however the improvement in tear strength becomes less pronounced although an improvement in selectivity is sustained even at lower levels. The improvements dependent upon addition of sulphite, are also influenced by the amount of delignifying agent (such as sodium hydroxide) present, the H Factor of the cook, and the species of lignocellulose being digested. Accordingly, in one form of the invention, sulphite addition within the range 0.1% to 15% may be used.

It is desirable however, that the sulphite addition be as low as practicable to simplify the pulping liquor chemical recovery, and for this reason, in a more preferred form of the invention a sulphite addition level of between 0.1% and 10% calculated as Na_2SO_3 addition by mass on oven dry wood is used.

It should be appreciated that the most economic amount of chemical to be used in the process of the invention will vary from mill to mill without affecting the basic discovery. For example, in order to obtain the most economic operation in a particular mill while preserving pulp strengths, the pulping rates, alkali requirements and time/termperature requirements will be taken into account, as these have been found to be interdependent, as is well known in the art.

We have found for example, that for an equivalent amount of redox agent, the sodium salt of tetrahydroanthraquinone is more effective than anthraquinone per se, although the difference may not be great, so that the choice of which redox agent to use would ultimately depend upon relative cost and availability in a particular location as more or less may be added to suit in order to obtain the desired effect.

In the present invention, the amount of redox agent to be used is within the range 0.01% by mass and 5% by mass calculation on the basis of the anthraquinone structure (not the derivative) and expressed as per cent on oven dry wood.

A preferred addition range of the redox agent is 0.01% to 2% by mass expressed as percent on oven dry wood of the anthraquinone structure.

With sulphite addition levels at least in the mid-range of those used in the present invention, the sulphite has an influence over the delignification rate as well as providing the improvement in strength properties, the delignification rate increasing with increasing amounts of sulphite so that less alkali need be employed for the same rate of delignification.

The alkali metal hydroxide used as the principal delignifying agent in the invention may also be varied to suit, and in accordance with normal pulpmill practise, and at least within the range 15% to 21% (expressed as NaOH on oven dry wood) has been found not to influence the tear strength of pulps made in accordance with the methods of the invention.

In one form of the invention alkali metal hydroxide within the range of 12% to 26% is used as the principal delignifying agent, the alkali metal hydroxide being expressed as per cent NaOH by mass on oven dry wood mass.

We have conducted experiments to explore and illustrate the inter-relationships between some of the main variables which may be encountered when applying the present invention to delignification in a particular pulpmill, as conditions and constraints will vary of course from one mill to another.

It will be appreciated that while a limited range of wood species may be used for pulping in any particular region, the present invention has application in many pulpmills throughout the world, and the potential range of species to be considered is therefore very large. For these reasons we illustrated the inter-relationships by way of example only, with reference to Figure 4 herein, using data obtained from our investigations from pulping Pinus radiata. The details and inter-relationship shown in Figure 4 will be self-evident to those skilled in the art of chemical pulping of lignocellulose. An inter-relationship between the amount of alkali metal hydroxide delignification agent and sulphite used in the pulping liquor, the H Factor used for the digestion and the pulp Kappa number resulting therefrom is shown. All of the digestions conducted to obtain the data shown in Figure 4 contained 0.5% anthraquinone (as SAQ) and even in the presence of this redox agent the influence of the sulphite on delignification (as indicated by the Kappa number) can readily be seen.

In the prior art neutral sulphite (NS/AQ) pulping a weak alkali such as sodium carbonate may be included in the pulping liquor for the purpose of providing a buffer for neutralizing wood acids and thereby to control pH of the pulping liquor. Although alkali metal hydroxide provides the principal delignifying agent in the present invention, buffer compounds such as sodium carbonate may be included if desired. In the two stage form of the invention for example, the first stage liquor may contain sodium carbonate to provide a buffer and thereby control pH.

Both the first and second stage liquors may contain any one or more of the alkali compounds selected from alkali metal hydroxides, alkali metal carbonates, alkaline earth metal hydroxides and alkaline earth metal carbonates, as may the liquor when only one stage is used, provided that the principle delignifying agent in at least one stage is one or more alkali metal hydroxide.

It will be appreciated that the liquor or liquors as the case may be, may contain other substances without departing from the scope of the invention provided that alkali metal hydroxide remains the principal delignifying agent preferably in combination with a preferred redox agent as defined hereinbefore.

Many chemical compounds have been proposed as additives in alkaline pulping. Some have been tested

together with anthraquinones and of these a few have been found to provide a technical improvement. None have been found to be commercially viable however, due to factors such as cost, availability and toxicity. Even anthraquinones, the most effective compounds found so far, are not particularly widely used as the margin between their cost and the benefits which they can provide is often difficult to find.

The most promising pulping process movement in recent years has been the introduction of anthraquinones and derivatives to the soda process, but at B. Bach and G. Fiehn found, the tear strength of the pulp is inferior to that of kraft, and this has imposed a serious commercial limitation on acceptance of their process.

Sulphite, particularly sodium sulphite is a relatively inexpensive non-toxic compound which can overcome the tear strength deficiency in the Soda/AQ pulping process to commercial advantage, while at the same time providing benefits to the process in addition to those provided by the preferred redox agents alone.

Claims

1. A pulping liquor for use in the digestion of lignocellulose, in the manufacture of lignocellulosic pulp, comprising an alkali metal hydroxide as a delignification agent and a sulphite, the sulphite being present in an amount of between 0.1 and 15% expressed as Na_2SO_3 by mass on oven dry mass of said lignocellulose.

2. A pulping liquor as claimed in claim 1 wherein the sulphite is present in an amount between 0.1 and 10%.

3. A process as claimed in claim 1 or claim 1 in which the liquor further contains a redox agent.

4. A pulping liquor as claimed in claim 3 in which the redox agent is selected from anthraquinone, anthrahydroquinone and homologues and derivatives thereof.

5. A pulping liquor as claimed in claim 4 in which the derivatives are selected from alkyl, alkoxy, hydroxy, amino, halo, sulphonate and carboxy derivatives of anthraquinone and anthrahydroquinone and hydrogenated forms thereof.

6. A pulping liquor as claimed in claim 3 in which the redox agent is selected from anthraquinone, anthrahydroquinone, anthraquinonemonosulphonate, tetrahydroanthraquinone and sodium or potassium salts thereof and tautomeric forms thereof.

7. A pulping liquor as claimed in any one of the preceding claims in which the alkali metal hydroxide is sodium hydroxide.

8. A pulping liquor as claimed in any one of the preceding claims wherein the sulphite is sodium sulphite.

9. In a process for producing lignocellulosic pulp in which lignocellulosic material is digested with an aqueous pulping liquor wherein the lignocellulose is treated with an alkali metal hydroxide as a principal delignification agent and with a sulphite wherein said sulphite is present in an amount of between 0.1 and 15% expressed as Na_2SO_3 by mass on oven dry mass of said lignocellulose.

10. A process as claimed in claim 9 in which the lignocellulose is treated with an aqueous pulping liquor containing both the alkali metal hydroxide and the sulphite.

11. A process as claimed in claim 9 in which the lignocellulose material is treated with the aqueous pulping liquor in two stages, the first treatment liquor containing the sulphite and the second treatment liquor containing the alkali metal hydroxide.

12. A process as claimed in any one of claim 9 to 11 in which the lignocellulose in which the pulping liquor additionally contains a redox agent.

13. A process as claimed in claim 11 in which one or both of the pulping liquors contain a redox agent.

14. A process as claimed in claim 12 or 13 in which the pulping liquor is as claimed in any one of claims 4 to 6.

15. A process as claimed in any one of claims 9 to 14 in which the hydroxide is sodium hydroxide.

16. A process as claimed in any one of claims 9 to 15 in which the sulphite is sodium sulphite.

17. A process as claimed in any one of claims 9 to 16 in which the lignocellulosic material is derived from a softwood or hardwood species.

18. A process as claimed in claim 17 in which the lignocellulosic material is a softwood.

19. A process as claimed in claim 17 in which the lignocellulosic material is in the form of chips.

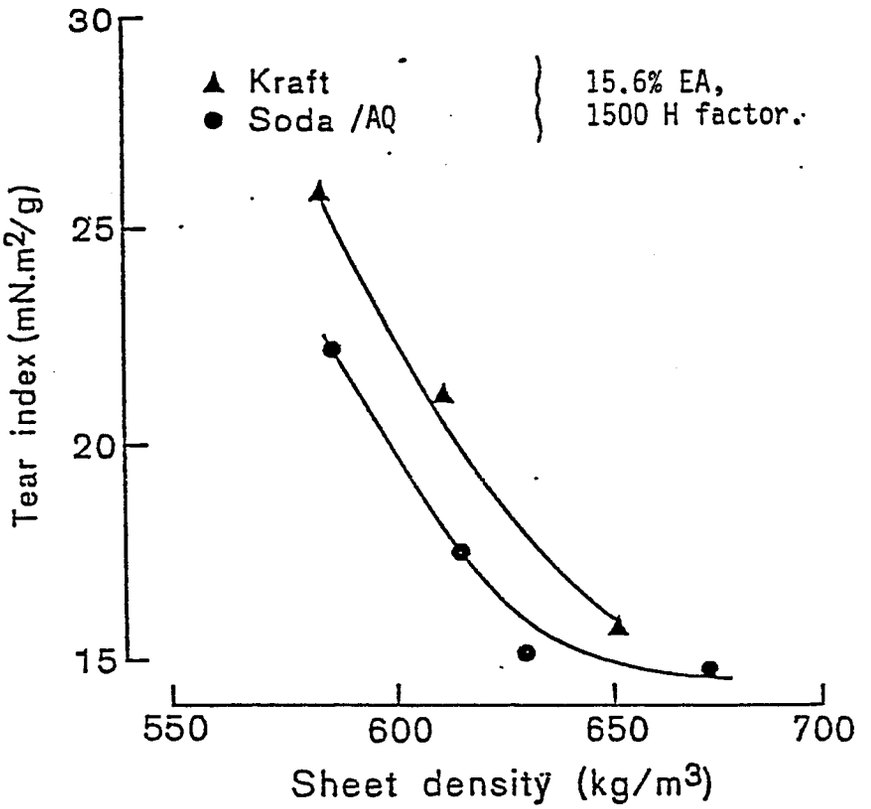

FIGURE 1

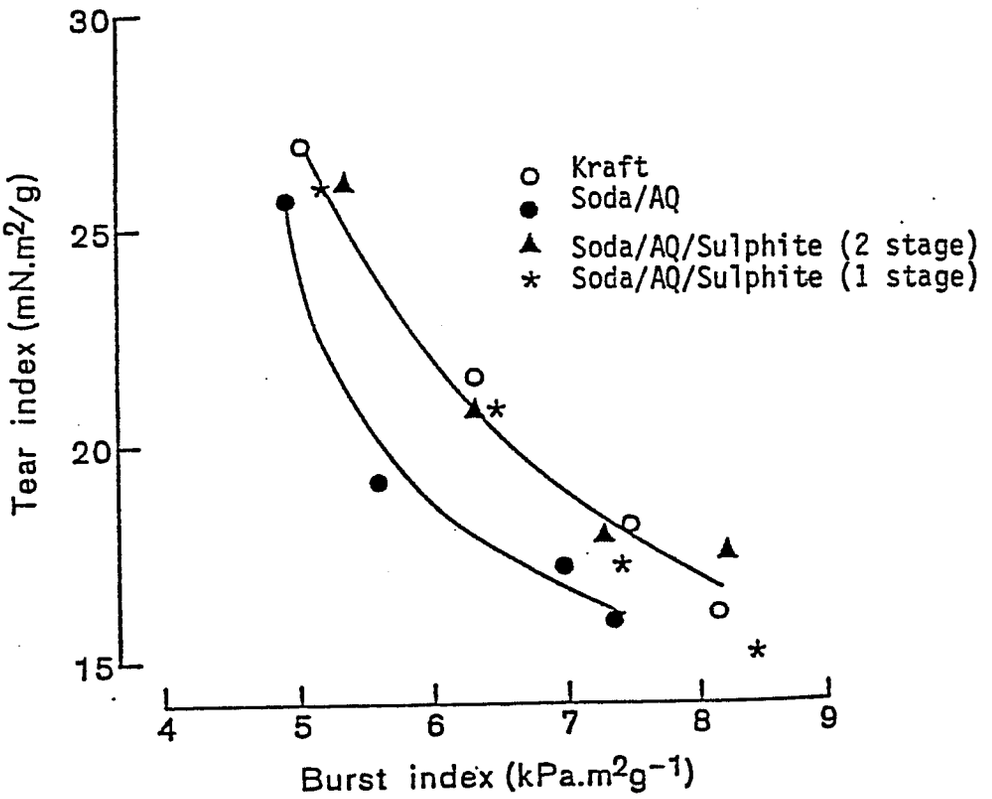

FIGURE 2

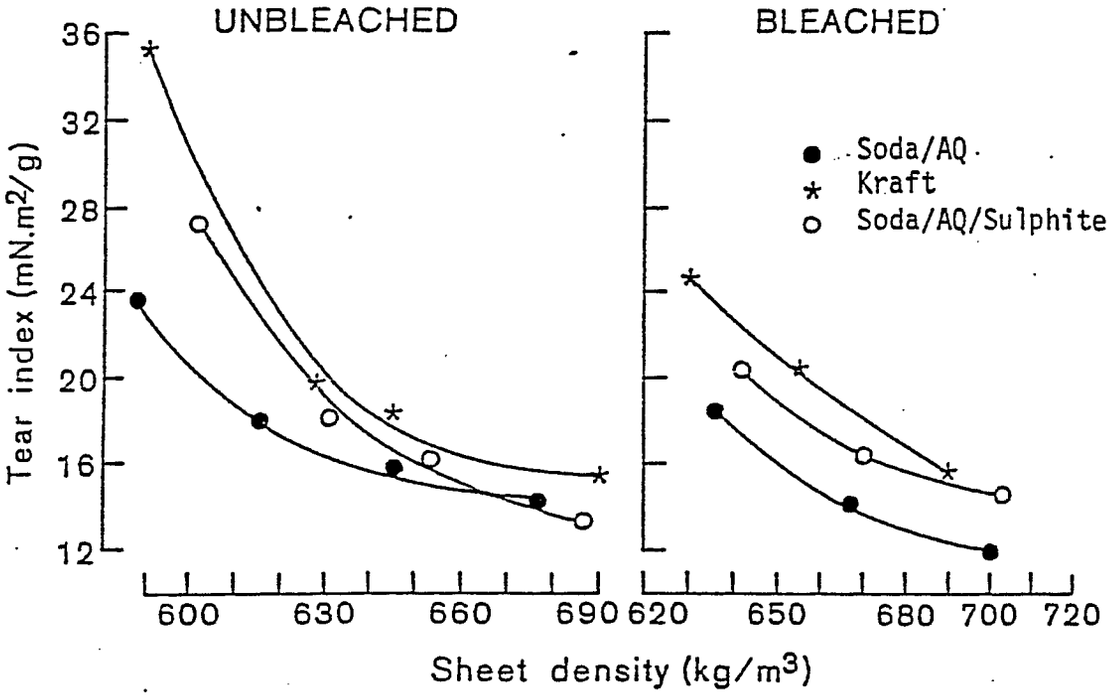

FIGURE 3

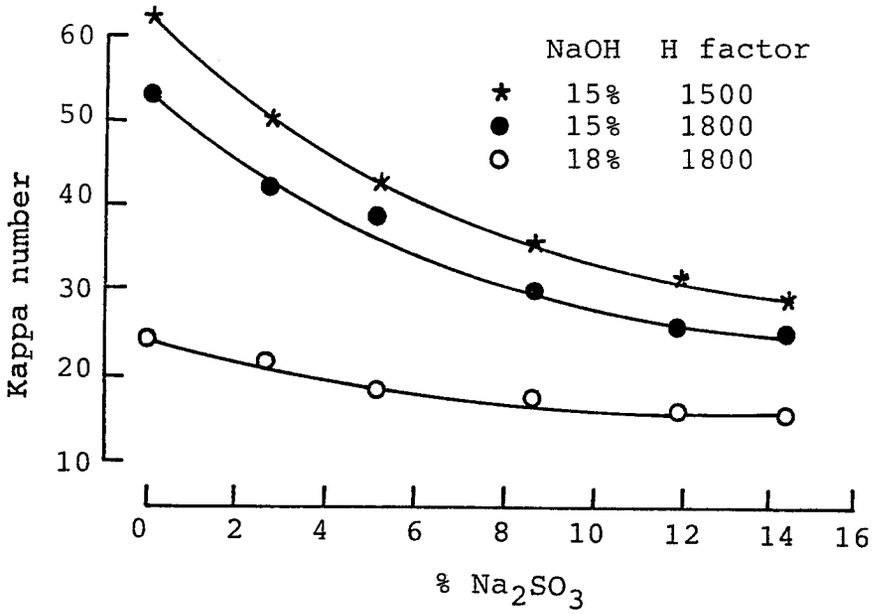

FIGURE 4