

PATENT SPECIFICATION

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(54) METHOD OF REMOVING PITCH OR RESIN FROM WOOD PULP

(71) We, PAPER INDUSTRIES CORPORATION OF THE PHILIPPINES, a Corporation of the Philippines, of Bislig, Surigao del Sur, in the Philippines, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of removing pitch or resin from wood pulp.

Wood contains resinous material which constitutes approximately 4—5% by weight of the trunk, varying somewhat in the sapwood and heartwood and in different species. In the sulphate process for the digestion of wood chips the cooking liquor is alkaline and normally contains sodium hydroxide (NaOH) which saponifies and dissolves most of the resins in the wood chips, the resins being removed from the pulp in the form of sodium salts dissolved in the spent liquor. However, in the ordinary sulphate process where no additives are added, some of the resins in the ray cells of the wood are left unattacked by the alkali and this resinous material is carried in colloidal suspension with the spent liquor. Since these particles are insoluble in water, spent black liquor or alkali, they remain attached to the fibres in the subsequent washing operation. Some of the dissolved resin which may be incompletely removed adheres to the pulp probably as a precipitate generally because of lowering of the pH value. These resin particles combine together and are carried with the pulp to the paper mill. Eventually, the particles agglomerate and adhere to the fourdrinier wire, suction boxes, presses, felts and calenders of the paper machine as a brownish, sticky and tacky mass. It is the precipitated material that is called pitch, and it is of complex composition and consists not only of wood resin but also of materials occluded during its precipitation.

Pitch in wood pulp is derived from the extraneous components of the wood and com-

prises to some extent a part or all of the extractives that are soluble in organic solvents. Pitch is undesirable in the paper making process because of its tendency to become separated from the fibres and to form deposits or lumps which may interfere with paper machine operations and which may be dispersed in the stock to form spots or cause holes in the finished paper or product.

Chemically, pitch is composed of at least twenty or more components, most of which are mixtures of fatty and resin acids, ketones and unsaponifiable organic substances which can be extracted with organic solvents such as alcohol and ether. The ratio of these natural pure substances or the combination of these are generally unknown and is immaterial since they can generally all be classified as pitch or resins.

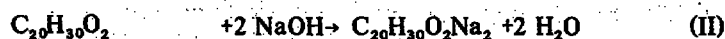
A fraction of the pitch components are semi-solid and tacky at about 20°C while the major portion melts at between 60°C to 100°C. Generally, pitch does not have a definite melting point and it is for this reason that it is difficult to control. These characteristics greatly favour pitch deposition on the paper machines as the above temperature ranges are easily obtained during the processing operation. Pitch deposits are often contaminated with other extraneous materials of the wood so that only a portion of the deposited pitch is soluble in organic solvents. The ether or petroleum ether extracts are generally soft and sticky and are often considered to represent the portion of total extractives responsible for pitch deposition. The extractives removed by ethanol following the ether extract are usually hard and non-tacky.

The present invention provides a method of removing pitch or resin from wood pulp to thereby inhibit the deposition of pitch or resin on the metal surfaces of equipment used in the processing of wood pulp and subsequent manufacture of paper products, which method comprises mixing with cooking liquor for the digestion of wood chips by the kraft or sulphate process copra or a veget-

- able oil or a fatty acid derivative thereof, cooking the resulting mixture with the wood chips in a digester or pressure vessel for pulping wood, and washing the resulting cooked wood pulp with water to remove the soluble pitch or resin derivatives from the wood pulp.
- Preferred substances which remove pitch or resin from wood pulp by the method according to the invention and thus inhibit the deposition of pitch or resin on the metal surfaces of equipment used in the processing of wood pulp and the subsequent manufacture of paper products are copra, coconut oil, palm oil, olive oil and corn oil and other vegetable oils or their fatty acid derivatives, either in their crude or refined form, or in admixture with other substances such as solvents, emulsifiers or other additives.



Glyceryl stearate + Alkali → Sodium stearate soap + Glycerol
present in coconut oil



Abietic acid + Alkali → Resin soap
present in resin.

- In furtherance of the above saponification reactions, the dissolution of the fatty acids in the form of sodium salts increases the micellar solubilization of the more or less hydrophobic constituents of the resins, i.e. unsaponifiables and remaining fatty acid esters. The surface active components of the stearin soaps formed induces the hydrophobic parts into the interior of the micelles enclosing the non-polar constituents of the resins and thereby releasing the resin. The released resin reacts with the excess alkali forming resin soaps. These resin soaps are held in suspension or emulsion by the stearin soaps and are made stable by the glycerol by-product formed in the first reaction.

- Copra, coconut oil, palm oil, olive oil and corn oil and other vegetable oils or their fatty acid derivatives act as softening and surface active agents which hasten the release of resin from the ray cells of the wood and solubilize unsaponifiable components of the resin. This is brought about by unsaponification of the glyceryl esters of these vegetable oils with the alkali of the cooking liquor. The soaps formed also act as protective colloids which tend to prevent agglomeration of resin particles and induce easy removal of soluble pitch derivatives by washing with water.

- The glycerol and glyceryl esters may also act as stabilizers by keeping the resin soaps in emulsifiable form and by preventing precipitation of the resin during sudden changes of pH while the pulp undergoes washing

Copra, coconut oil, palm oil, olive oil and corn oil and other vegetable oils or their fatty acid derivatives not only remove pitch or resin from wood pulp but also prevent the formation of both the soft, sticky and the hard, non-tacky fractions of pitch.

Copra, coconut oil, palm oil, olive oil and corn oil and other vegetable oils or their fatty acid derivatives contain glyceryl esters of the higher fatty acids (palmitic, lauric and stearic) which when mixed with the cooking liquor (alkali) during the digestion of wood form stearin soaps and glycerol by-products. At the same time, the abietic acid present in the resin of the wood reacts with the alkali forming resin soaps. These reactions may be briefly summarized as follows:

operations. This is especially important in preventing deposition of pitch on the surfaces of process equipment and in preventing or minimizing precipitation of dispersed resin onto the fibers.

The pulp is thus freed from soluble resins and pitch by a series of washing operations preferably with hot water.

The following is the outline of the procedure for using copra, coconut oil, palm oil, olive oil and corn oil and other vegetable oils or their fatty acid derivatives in the digestion of wood employing the kraft or sulphate process. In the sulphate process, the active chemicals of the cooking liquor are sodium hydroxide (NaOH) and sodium sulphide (Na₂S). The amount of active alkali charge of a normal kraft cook is about 10% to 20% of the bone dry weight of chips used. However, this amount may vary in some mills due to the different wood species being cooked.

The cooking liquor of a normal kraft charge contains about 155 kgs. of active alkali (calculated as Na₂O) per ton of bone dry wood, and is made up of white liquor, containing the main part of the active chemicals, and black liquor, which is the liquor from a previous cook containing organic substances and consumed chemicals and which is used as diluent to ensure good liquor circulation without introducing extra water. However, in some mills, fresh water may be used as diluent to product pulp of a lighter colour.

The cook is carried out inside a digester

or pressure vessel which is heated either by direct or indirect steam usually at a pressure generally up to 140 psi and at temperatures up to 180°C for a period of as long as five hours. However, for purposes of this invention, the copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oil or their fatty acid derivatives are applicable to any of the operating conditions outside of the normal kraft cook mentioned in the foregoing discussion inasmuch as the copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oil or their fatty acid derivatives react almost completely as soon as heated and proceed to complete saponification within a short period. Hence, copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oil or their fatty acid derivatives are applicable to kraft cooks of mild or moderate nature. On the other hand, the vegetable oils can be of decided advantage to kraft cooks requiring a longer period of cooking and necessitating elevated temperatures and pressures because these conditions greatly increase the surface action and enhance the emulsifying action of the soaps formed in the reaction.

To illustrate the use of copra, coconut oil, palm oil, olive oil or corn oil or any other vegetable oil in a typical digester the following procedure may be followed which is applicable to all types of digesters and to all kinds of cooks employing the kraft or sulphate process.

The digester is charged with the calculated amount of cooking liquor (alkali) required to make a full cook. A measured volume of crude or refined copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their fatty acid derivatives in an amount of from 0.1% to 5.0% by weight of the bone dry weight of chips is then run in and mixed with the cooking liquor. The amount of the copra or vegetable oil may be varied in a process to less than 0.1% where the resin content (extractives) of the wood chips is below 2%. On the other hand for wood species that have higher resin contents, an amount of coconut oil greater than 0.5% may be necessary. For other products in which copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their fatty acid derivatives have been diluted or mixed with other components such as solvents, emulsifiers and other additives, the dosage will have to be slightly higher and this will depend on how much copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their derivatives are actually present in the product.

After the copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their derivatives are mixed with the white liquor, a calculated amount of black liquor diluent taken from a previous cook is added to dilute the cooking liquor in order to obtain the

necessary liquor to wood ratio. The required volume of wood chips is then charged into the digester and the digester cover is closed. The sequence of charging the cooking liquor, copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their derivatives, black liquor and wood chips is immaterial. The copra or vegetable oil may be added first or may be put in last to be charged into the digester. However, for stationary type of digesters it is preferable that the copra or vegetable oil be mixed with the cooking liquor during charging.

The cook is started by introducing steam. Usually, the steam valve is opened gradually so that the vessel pressure builds up gradually and the temperature rises smoothly. However, the operating conditions such as pressure, temperature, time to temperature, and time at temperature (retention time), may vary at different mills, but this will not in any way affect the action of copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their derivatives and conditions below or above the normal kraft cook will not alter the reaction of the copra or vegetable oils or their fatty acid derivatives and alkali inside the digester or pressure vessel.

During the cooking period, a series of reactions take place inside the digester. The initial action of the alkali is believed to be on the lignins of the wood. This is known as delignification, which probably involves replacement of the hydroxyl groups by alkali-unstable mercaptan groups which are then converted into sulfide groups. The second step involves hydrolytic splitting of the molecule in the presence of the alkali, forming free phenolic hydroxyl groups which make the lignin soluble in alkali.

The second reaction is probably dissolution of some of the carbohydrates. This involves solvation of the hydroxyl groups by the hydroxyl ions of the cooking liquor. At this stage of cooking, side reactions possibly take place between the excess alkali and the copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their fatty acid derivatives, resulting in the formation of saponified compounds of stearin soap and glycerol according to reaction (I) previously described. The saponified stearin soaps facilitate swelling of the cell walls which hastens penetration of the cooking liquor and diffusion of chemicals from the outer to the inner wall. This phenomenon caused by the copra, coconut oil, palm oil, olive oil or corn oil or other vegetable oils or their fatty acid derivatives is of considerable importance in allowing easy penetration and diffusion of chemicals in all directions in order to ensure uniformity of cook and clean blow.

The saponified stearin soaps on further boiling act as surface active agents which soften

(B)

5 and penetrate the epithelial or ray cells of
the wood, causing the release of resin. The
active alkali then reacts with the released
resin forming resin soaps according to reac-
10 tion (II) previously described. The action
of alkali on the resins of the wood and its
removal from the ultimate fibers is known
as deresination. Deresination is of prime im-
15 portance in pitch removal and control because
if not effectively carried out as in the case
of the ordinary kraft cook without the use of
copra, coconut oil, palm oil, olive oil or corn
oil or other vegetable oils or their fatty
20 acid derivatives some of the resins may not
be released from the epithelial or ray cells
and remain unattacked by the alkali. These
resin particles cling to the fibers because of
the adhesive properties of the resins. They
are separated and/or dispersed only after the
beating or refining operations, and as they
continue to agglomerate they eventually form
a sticky solid mass which is called pitch.

25 At this point, it is interesting to note that
the products formed by the reaction of copra,
coconut oil, palm oil, olive oil or corn oil
or other vegetable oils or their fatty acid
derivatives are surface active agents in nature
which soften and penetrate the ray cells of
30 the wood causing the release of resins. Thus,
the copra or vegetable oils or their fatty
acid derivatives ensure effective deresination
through surface action and at the same time
act as protective colloids to effect thorough
35 removal of saponified resins and soluble pitch
derivatives.

40 After the end of the retention period, the
cooked pulp from the digester is blown into
a blow tank by release of pressure. From the
blow tank, the pulp slurry containing black
liquor carrying the pitch or resin in solution
is pumped into knotters and screens to separ-
ate the uncooked stuff (knots) and rejects

from the fine fibers (accepts). The accepts
from the secondary screen then go to a first
brown stock washer for separation of the
45 black liquor while still hot from the pulp to
effect removal of soluble pitch derivatives.
This operation is carried out by passing the
pulp slurry to a rotary drum vacuum washer.
50 The pulp or brown stock is pumped to a
second brown stock washer and finally to a
third brown stock washer for washing to
remove traces of black liquor from the pulp.
The pulp when properly and effectively washed
55 appears light brown and if squeezed should
impart a very slight brownish tinge to the
filtrate.

The pulp thus discharged from the third
brown stock washer is completely or almost
completely free from soluble pitch derivatives
60 and is ready for paper making.

Pulp obtained from an ordinary kraft cook
without copra, coconut oil, palm oil, olive oil
or corn oil or other vegetable oils or their
fatty acid derivatives added is not thoroughly
65 deresinated and usually leaves some pitch de-
posits on the fourdrinier wires, suction boxes,
presses, dryers and calenders of the paper
machine. However, pulp obtained from a kraft
cook with copra, coconut oil, palm oil, olive
70 oil or corn oil or other vegetable oils or
their fatty acid derivatives if properly washed
will not leave any pitch residues on the sur-
faces of paper mill equipment.

75 Given below are results of experimental
cooks using varying dosages of copra, coconut
oil, palm oil, olive oil or corn oil or their
fatty acid derivatives. Extractives of wood
chips before cooking and extractives of pulp
after cooking and washing were determined
80 to evaluate the effect of copra, coconut oil,
palm oil, olive oil or corn oil or their fatty
acid additives in removing pitch or resin
from pulp.

TABLE I

Date	Cook No.	% Coconut Oil Used	% Extractives (Original) Chips	% Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
9/ 8/72	62	5.0	5.31	0.905	82.96
9/20/72	71	4.0	4.149	0.815	80.40
9/20/72	72	3.0	4.149	0.470	88.60
9/21/72	73	2.0	4.149	0.80	80.70
9/22/72	74	1.0	4.149	1.275	69.3
9/25/72	76	None	2.109	1.03	51.0 (Control)
10/ 2/72	81	1.0	2.685	0.270	89.6
10/31/72	98	0.5	1.74	0.175	89.90
11/ 1/72	100	0.5	1.74	0.52	70.01
11/ 4/72	103	0.5	2.48	0.535	78.42
11/ 4/72	104	0.5	2.48	0.625	74.80
11/11/72	108	0.5	2.545	0.50	80.40
11/29/72	125	0.5	2.03	0.22	89.16

TABLE II

Date	Cook No.	% Copra	% Extractives (Original) Chips	% Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
10/30/73	274 (Pilot)	None	2.31	1.27	44.2 (No copra)
11/ 5/73	281 (Pilot)	0.5	2.31	0.89	61.5
11/ 5/73	282 (Pilot)	1.0	2.31	0.61	73.5
12/10/73	303 (Pilot)	0.5	2.77	0.71	74.0
12/ 6/73	Mill Run	0.5	2.41	0.87	63.8
12/ 6/73	-do-	0.5	3.41	1.03	70.0
12/ 6/73	-do-	0.5	3.41	1.02	70.1
12/ 7/73	-do-	0.5	2.68	0.77	71.0
12/ 7/73	-do-	0.5	2.68	0.64	76.1
12/ 7/73	-do-	0.5	2.68	0.91	66.2

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TABLE II A

Date	Cook No.	% Fatty Acid Derivatives	% Extractives (Original) Chips	% Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
12/ 4/73	297 (Pilot)	None	2.77	1.56	43.7 (No Fatty Acids)
12/ 5/73	299 (Pilot)	0.2	2.77	0.64	76.5
12/ 5/73	300 (Pilot)	0.5	2.77	0.54	80.1
12/ 7/73	301 (Pilot)	0.5	2.77	0.55	80.0
1/25/74	Mill Run	0.5	3.47	1.12	67.6
1/25/74	-do-	0.5	2.70	0.81	70.0
1/27/74	-do-	0.5	2.70	0.95	64.8
1/27/74	-do-	0.5	2.08	0.69	66.9
1/27/74	-do-	0.5	2.68	0.84	68.8
1/28/74	-do-	0.5	2.33	0.82	65.0
1/28/74	-do-	0.5	2.33	0.86	63.3

TABLE III

Date	Cook No.	% Olive Oil	% Extractives (Original) Chips	% Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
2/ 5/74	337	0.5	2.37	0.83	65.0
2/ 5/74	338	0.5	2.37	0.31	86.9

TABLE IV

Date	Cook No.	% Corn Oil Fatty Acids	% Extractives (Original) Chips	% Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
8/ 2/74	418	0.5	1.47	1.07	27.2
8/ 3/74	419	0.5	1.47	0.99	32.7
8/ 4/74	420	0.5	1.47	1.09	26.0

TABLE V

Date	Cook No.	% Palm Oil	% Extractives (Original) Chips	Extractives (Pulp)	% Pitch or Resin (Extractives) Removed
8/14/74	438	0.5	1.49	0.84	43.6
8/15/74	439	0.5	1.49	1.22	18.1

From the results given above, pitch or resin (extractives) removed from original chips with the use of coconut oil may be as high as 89%, compared to only 51.0% without the addition of coconut oil (see cook No. 76).

The following table also shows the effect of coconut oil on reducing and/or eliminating "Downtime" in order to clean and remove pitch or resin deposits from the fourdrinier wire cloth, presses, rolls, felts and calendars of paper machines.

Total Downtime (Hours) For Cleaning Off Pitch Deposits From Paper Machine Systems

Month	Newsprint Machine	Kraft Machine
June, 1972	51.17	23.12
July, 1972	37.67	30.12
Aug., 1972	10.58	5.97
Sept., 1972	17.33	21.92
Oct., 1972	9.67	None
Nov., 1972	None	None

Note: Sept. 23, 1972—Started use of coconut oil as pitch control agent and defoamer in Reitiner Groundwood Pulp Mill (RGP).

Sept. 29, 1972—Started use of coconut oil as pitch control additive in Kraft Pulp Mill digester cooks.

Evaluation: (I) Average Monthly Downtime

A. Newsprint Machine

1. Before coconut oil was used=29.19 hours
2. After coconut oil was used = 4.84 hours

B. Kraft Machine

1. Before coconut oil was used=20.31 hours
2. After coconut oil was used = 0

(II) Reduction in Machine Average Monthly Downtime After Coconut Oil Usage

$$A. \text{ Newsprint Machine} = \frac{29.19 - 4.84}{29.19} \times 100 = 83.41\%$$

$$B. \text{ Kraft Machine} = \frac{20.31 - 0}{20.31} \times 100 = 100.00\%$$

Note: Above evaluation covers observations from month of June, 1972. This is due to the fact that pitch control system was organized in June, 1972.

WHAT WE CLAIM IS:—

- 15 1. A method of removing pitch or resin from wood pulp to thereby inhibit the deposition of pitch or resin on the metal surfaces of equipment used in the processing of wood pulp and subsequent manufacture of paper products, which method comprises mixing with cooking liquor for the digestion of wood chips by the kraft or sulphate process copra or a vegetable oil or a fatty acid derivative thereof, cooking the resulting mixture with the wood chips in a digester or pressure vessel for pulping wood, and washing the resulting cooked wood pulp with water to remove the

soluble pitch or resin derivatives from the wood pulp.

2. A method as claimed in Claim 1 wherein the vegetable oil is coconut oil, palm oil, olive oil or corn oil.

3. A method as claimed in Claim 1 or 2 wherein the copra or vegetable oil is employed in an amount of from 0.1 to 5.0% based on the bone dry weight of the wood chips.

4. A method as claimed in any of Claims 1 to 3 wherein the said resulting mixture and the wood chips are cooked at a pressure up to 140 p.s.i. and at a temperature up to 180°C for up to five hours.



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4. A method as claimed in any of Claims 1 to 3 wherein the said resulting mixture and the wood chips are cooked at a pressure up to 140 p.s.i. and at a temperature up to 180°C for up to five hours.

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5. A method according to Claim 1 of removing pitch or resin from wood pulp substantially as herein described.

6. Wood pulp from which pitch or resin
5 has been removed by the method claimed in any of Claims 1 to 5.

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* C L M S *