

[54] **METHOD OF IMPROVING SMELT PROPERTIES AND REDUCING DISSOLVING TANK EXPLOSIONS DURING PULPING OF WOOD WITH SODIUM BASED LIQUORS**

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[22] Filed: **Oct. 15, 1973**

[21] Appl. No.: **406,498**

[52] **U.S. Cl.**..... **162/30, 162/36, 266/26**

[51] **Int. Cl.**..... **D21c 11/12**

[58] **Field of Search**..... **162/29, 30, 36; 423/207; 266/26**

[56] **References Cited**

UNITED STATES PATENTS

3,447,895	6/1969	Nelson et al.	162/30 X
3,615,175	10/1971	Nelson	162/30 X
3,650,889	3/1972	Fogman	162/30

OTHER PUBLICATIONS

Nelson et al., "What Causes Kraft Dissolving Tank Ex-

plosions," Paper Trade Journal, (7/16/56), pp. 50-56.

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[57]

ABSTRACT

Lithium hydroxide, potassium hydroxide, lithium carbonate, potassium carbonate, and alkali metal borates or mixtures thereof can be added to the smelt produced by pulping wood with a sodium based liquor containing such compounds as sodium carbonate and sodium hydroxide to lower the melting point and make the smelt softer and more fluid so that when it enters the dissolving tank violent explosions are substantially eliminated. These additives do not interfere with pulping and paper strength is not affected by their use.

13 Claims, No Drawings

METHOD OF IMPROVING SMELT PROPERTIES AND REDUCING DISSOLVING TANK EXPLOSIONS DURING PULPING OF WOOD WITH SODIUM BASED LIQUORS

BACKGROUND OF THE INVENTION

Molten smelt and water are a hazardous combination of compounds which are present in large quantities in a wood pulping mill. When such smelt mixes with water in an uncontrollable manner, violent explosions can occur. These explosions can take place in the recovery furnace when a boiler tube breaks and water comes into contact with molten smelt at the bottom of the furnace. Dissolving tank explosions occur when molten smelt contacts the water or green liquor in the dissolving tank. Both of these explosions are extremely hazardous and have been a continuing concern to the paper industry for many years. The dissolving tank explosions, while perhaps not posing as serious a threat to closing down a mill as a boiler explosion, nevertheless are an ever present threat to the safety of operating personnel and have forced cessation of mill operations in the past. It is the prevention and control of dissolving tank explosions to which the present invention is primarily directed.

In 1955, John Sallack carried out an investigation of explosions in the soda smelt dissolving operation and reported his results in *Pulp and Paper Magazine of Canada*, 59, 114 (1955). He found that the temperature and composition of the dissolving liquor in a straight soda pulping operation influenced the severity of the smelt-water reaction in that higher temperature resulted in less violence of quenching as did the use of pure water as compared to the pulping liquor containing dissolved salts. It was established that the addition of more than 5% NaCl or 10% NaOH to the smelt consistently produced explosions whereas pure Na_2CO_3 was not explosive. Thus, the physical state of the smelt was found to be important and the author suggested shattering the molten smelt stream with steam jets prior to entering the dissolving tank. Apparatus to accomplish such shattering is described in U.S. Pat. No. 2,831,753.

In 1956, Nelson and Kennedy reported on what causes kraft dissolving tank explosions in *Paper Trade Journal*, July 16, 1956, pages 50-56 and confirmed Sallack's observations on the relationship between smelt composition and temperature. The authors stressed the importance of the physical characteristics of the smelt and especially the size of the molten smelt particles under the surface of the liquor. It was concluded that if the molten smelt is present in the form of small spheres, it does not explode when quenched with water. However, if the smelt is not flowing from the furnace in a steady stream the usual shattering device is inadequate to prevent the dissolving tank explosions which result when a molten globule falls from the furnace spout into the tank. The prevention of the freezing up of the smelt and the maintenance of a steady flow of molten smelt by other than physical means is the principal object of this invention.

SUMMARY OF THE INVENTION

In its broadest aspects, the present invention involves the addition of an alkali metal compound preferably alkali metal hydroxides, carbonates and borates or mixtures thereof (other than sodium carbonate) to a so-

dium based smelt produced from a wood pulping process in an amount sufficient to lower the melting point of the original smelt to improve molten smelt fluidity and prevent smelt spout plugging as well as dissolving tank explosions. In addition, the smelt is softer and can be more readily removed from the spout if solidification does occur. More specifically, this invention is concerned with chemical means for improving the properties of sodium carbonate smelt produced from a nonsulfur wood pulping process such as one utilizing sodium carbonate and sodium hydroxide as the cooking liquor. Sodium carbonate smelts in particular require higher temperatures to prevent them from solidifying in the furnace compared to smelts containing sulfur produced by kraft or neutral sulfite semichemical processes.

GENERAL DESCRIPTION OF THE INVENTION

The depression of the melting point of a pure compound by adding a second component is a well known scientific fact. However, more than just lowering the melting point is involved in adding chemicals to a smelt produced in a wood pulping process. For example, any chemical which is added must be non-explosive, non-corrosive, water soluble, economical, recoverable and above all, compatible with the other constituents in the pulping liquor and not detrimental to the pulp properties. It has now been found that only a limited number of compounds meet the desired requirements. These compounds include lithium carbonate, lithium hydroxide, sodium hydroxide, potassium carbonate, potassium hydroxide, potassium borate, sodium borate and lithium borate. Of these, the preferred compounds are potassium carbonate, potassium hydroxide and sodium borate.

The chemicals employed to decrease the melting point of the smelt are used in various concentrations. In general, any potassium containing compound can be used and preferably non-toxic compounds. Thus, the alkali metal hydroxides and carbonates are used in concentrations of from 1 to 80 mole percent based on Na_2O but the maximum effect of K_2CO_3 is achieved at about 40 mole percent which lowers the melting point of Na_2CO_3 smelt about 280°F compared to the melting point of $1,593^\circ\text{F}$ for 100% Na_2CO_3 smelt. Since KOH is very similar to NaOH, it is converted to K_2CO_3 in the recovery process and is effective at the same concentrations. Borax, on the other hand, can be used in lower concentrations on the order of from 2 to 10 mole percent based on Na_2O . Thus, 10 mole percent of borax lowers the melting point of pure Na_2CO_3 smelt about 500°F to $1,093^\circ\text{F}$. In these concentrations, smelt fluidity is optimized whereas smelt spout plugging and dissolving tank explosions are minimized.

The chemicals employed in the present method of improving smelt properties and reducing dissolving tank explosions can be added at any point in the liquor cycle but preferably where good control is available such as in the white liquor make up tank or in the black liquor tank. It is only necessary that the smelt contain an amount of such chemicals sufficient to lower the melting point of the smelt so that stoppage does not occur due to a build-up of solid smelt prior to entering the dissolving tank.

By employing the chemicals described hereinbefore in the concentrations noted, several benefits result such as (1) fluidity of the smelt increases thus preventing

major plugging of the spout from the furnace and the resulting dissolving tank explosions when the plug is knocked off and a surge of smelt discharges from the furnace (2) there are no adverse effects on the pulp properties or paper produced therefrom (3) the chemical compounds used do not sensitize the sodium carbonate smelt (4) alkali metal salts existing in the pulping liquor after the digesting operation are so efficiently removed that very little make-up chemical is required (5) chemical costs are substantially the same as when only sodium compounds are used in the cooking liquor and (6) fuel savings are appreciable.

Although the examples which follow are based upon the substitution or addition of various amounts of K_2CO_3 , KOH or borax in a cooking liquor containing a mixture of NaOH and Na_2CO_3 which otherwise would produce a 100% Na_2CO_3 smelt it is to be understood that the conditions and amounts of chemicals are not to be limited thereto but that substantially the same desirable results are obtained when one employs the specified conditions or other chemicals hereinbefore enumerated to lower the melting point of a sodium based smelt.

THE PREFERRED EMBODIMENTS

EXAMPLES 1 - 11

Hardwoods containing 35% aspen were pulped using a cooking liquor containing 85% by weight of sodium carbonate and 15% by weight of sodium hydroxide both based on Na_2O . Each cook consisted of 2,000 grams of hardwood chips on an oven dried basis. Various amounts of K_2CO_3 and KOH were substituted for the Na_2CO_3 and NaOH of the standard cook and various amounts of borax were added thereto for comparison with the standard cook which used 5% by weight of total chemical expressed as Na_2O . A liquor to wood ratio of 6 to 1 was used and each cook was heated to 340°F. within 50 minutes and held there for another 45 minutes. The cooked chips after each treatment were then defibered and the resulting pulp refined to 450 Canadian Standard Freeness. The refined pulp was converted into handsheets and the properties of the paper determined at 26 pounds per thousand square feet by standard procedure. The conditions employed, pulp yield obtained and the strength properties of the sheets are shown in the table below wherein ring crush is expressed in pounds per 6 inches of sample length, tear in grams per 16 sheets, tensile in pounds per 1 inch width, corrugating medium test (CMT) in pounds per 10 flutes and additive as percent of total chemical expressed as Na_2O .

Additive & % Total Chemical	Pulp Yield %	Ring Crush	Tear	Tensile	CMT
Standard	74.1	59	70	31.8	49.6
Standard	76.9	63	72	31.5	55.7
Standard	79.7	60	70	33.0	56.0
Borax 2.7	76.2	67	72	30.3	45.3
Borax 5.2	77.0	61	72	33.0	58.4
K_2CO_3 10	75.2	57	73	31.1	51.6
K_2CO_3 25	77.1	59	69	30.8	52.9
KOH+ K_2CO_3 20	77.0	59	70	30.7	48.8
KOH+ K_2CO_3 35	74.8	63	66	29.6	47.6
KOH+ K_2CO_3 50	76.5	64	69	30.1	51.2

From the foregoing data, it is apparent that the yield and physical properties of the corrugating medium are

not significantly affected when various amounts of borax, K_2CO_3 and KOH are used in the cooking liquor compared to the standard cooking liquor containing only NaOH and Na_2CO_3 . In each instance where an additive was employed, the smelt temperature was drastically reduced and dissolving tank explosions were diminished or eliminated.

EXAMPLE 11

In actual mill operations using a cooking liquor comprising only sodium hydroxide and sodium carbonate with no additive to lower the melting point of the smelt resulting therefrom, the smelt solidified in the recovery furnace spout, formed icicle-like projections 4 to 5 feet long which hung from the spout into the dissolving tank, plugged the spout hole and caused the molten smelt to solidify to a dangerous level in the furnace. Frequent plugging of the spout occurred requiring acetylene torches and a jack hammer to melt and chisel the solidified smelt off the spout and to open the spout hole. During the chiseling operation, large chunks of smelt fell into the dissolving tank and upon contact with the water exploded violently which was extremely hazardous to the mill personnel. Over a period of 30 days, about 100 spout pluggings occurred.

When potassium carbonate, borax, potassium hydroxide or mixtures thereof were added to the cooking liquor in the amounts specified in the preceding examples, only 14 spout pluggings occurred during the same period of time. The additives kept the smelt soft and any accumulation usually fell off the spout unassisted in small chunks before any significant build-up took place. Whenever one of the infrequent pluggings did occur, the spout was readily cleared by piercing the smelt with a metal lance.

If desired, other compounds such as lithium carbonate or potassium borate may be substituted for the compounds used in the examples with equally good results. All the compounds previously enumerated will lower the melting point of the smelt to keep it flowing smoothly into the dissolving tank and thus prevent smelt solidification and the devastating explosions which have occurred in the past when huge particles of smelt contacted the water in the dissolving tank. Concentrations of the compounds used to improve smelt properties can vary widely up to 80% based on Na_2O but for economic reasons a range of from 10 to 50% is preferred.

It will be apparent to those skilled in the art of wood pulping and chemical recovery that the same techniques herein described can be used advantageously in other types of chemical recovery processes and particularly those employing a fluidized bed.

What I claim is:

1. In a cyclic pulping and chemical recovery process for producing paper pulp from ligno cellulosic materials utilizing an aqueous sodium based cooking liquor at elevated temperatures and pressures wherein the aqueous filtrate is separated from the pulp by washing, then concentrated and ignited in a recovery furnace to form a smelt which is dissolved in water and reconstituted for further use, the improvement which comprises adding an alkali metal compound selected from the group consisting of LiOH, KOH, Li_2CO_3 , K_2CO_3 and alkali metal borates or mixtures thereof to the pulping cycle in an amount sufficient to lower the melting point of

the smelt to improve smelt fluidity and reduce dissolving tank explosions.

2. A process as in claim 1 in which the alkali metal compound added is potassium carbonate.

3. A process as in claim 1 in which the alkali metal compound added is lithium carbonate.

4. A process as in claim 1 in which the alkali metal compound added is potassium hydroxide.

5. A process as in claim 1 in which the alkali metal compound added is an alkali metal borate.

6. A process as in claim 5 in which the alkali metal borate is borax.

7. A process as in claim 5 in which the alkali metal borate is potassium borate.

8. A process as in claim 5 in which the alkali metal borate is added in a concentration of from 2 to 10 mole percent based on sodium oxide.

9. A process as in claim 1 in which the lithium and

potassium hydroxides and carbonates are added in a concentration of from 1 to 80 mole percent based on sodium oxide.

10. A process as in claim 1 in which the lithium and potassium hydroxides and carbonates are added in a concentration of from 5 to 50 mole percent based on sodium oxide.

11. A process as in claim 1 in which the sodium based cooking liquor is a mixture of 20% by weight of sodium hydroxide and 80% by weight of sodium carbonate based on sodium oxide.

12. A process as in claim 11 in which from 10 to 25% of K_2CO_3 based on Na_2O is substituted for the NaOH and Na_2CO_3 .

13. A process as in claim 11 in which from 20 to 50% of KOH and K_2CO_3 based on Na_2O is substituted for the NaOH and Na_2CO_3 .

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