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[54] **ANALYSIS OF KRAFT LIQUORS**
5 Claims, 2 Drawing Figs.

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253; 324/30 B

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ABSTRACT: Kraft cooking liquors used in the pulping of wood are analyzed for apparent causticity by utilizing conductivity measurements taken before and after precipitation of the soluble carbonates in the liquors. The differential conductivity determined correlates directly with the apparent causticity of the cooking liquor.
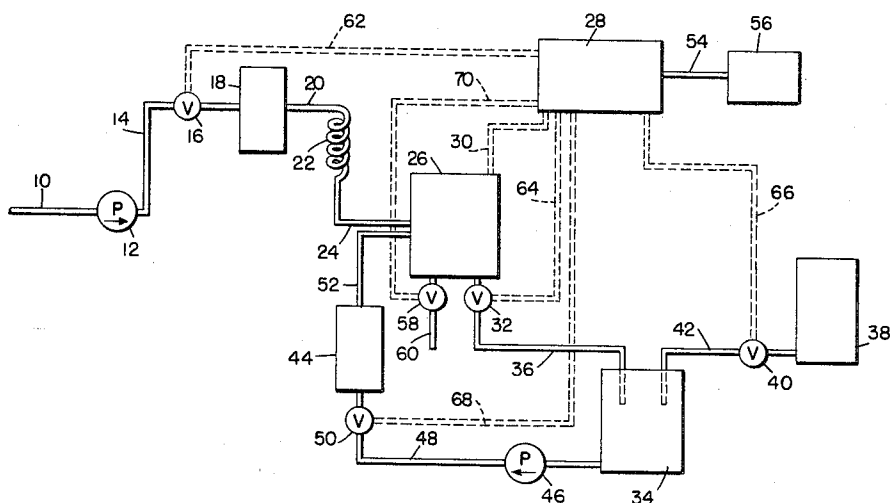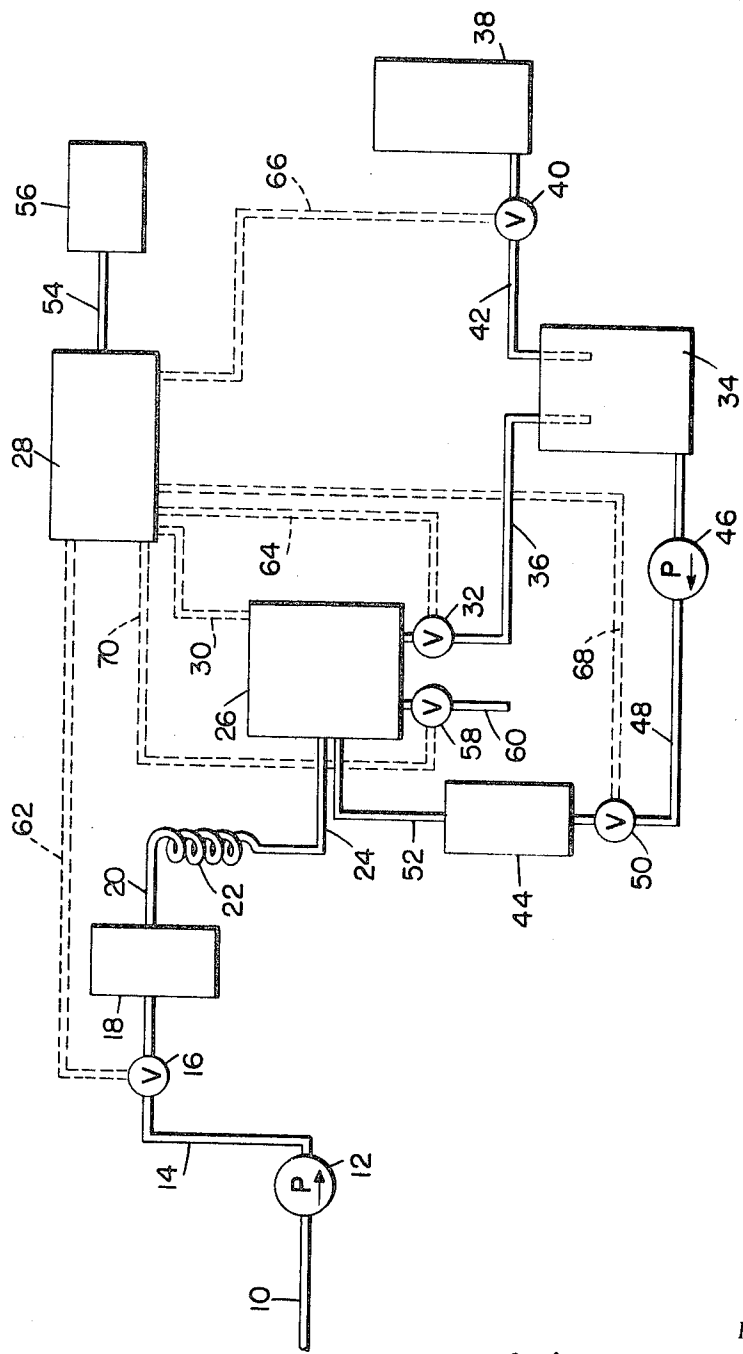
FIG. 1

INVENTOR

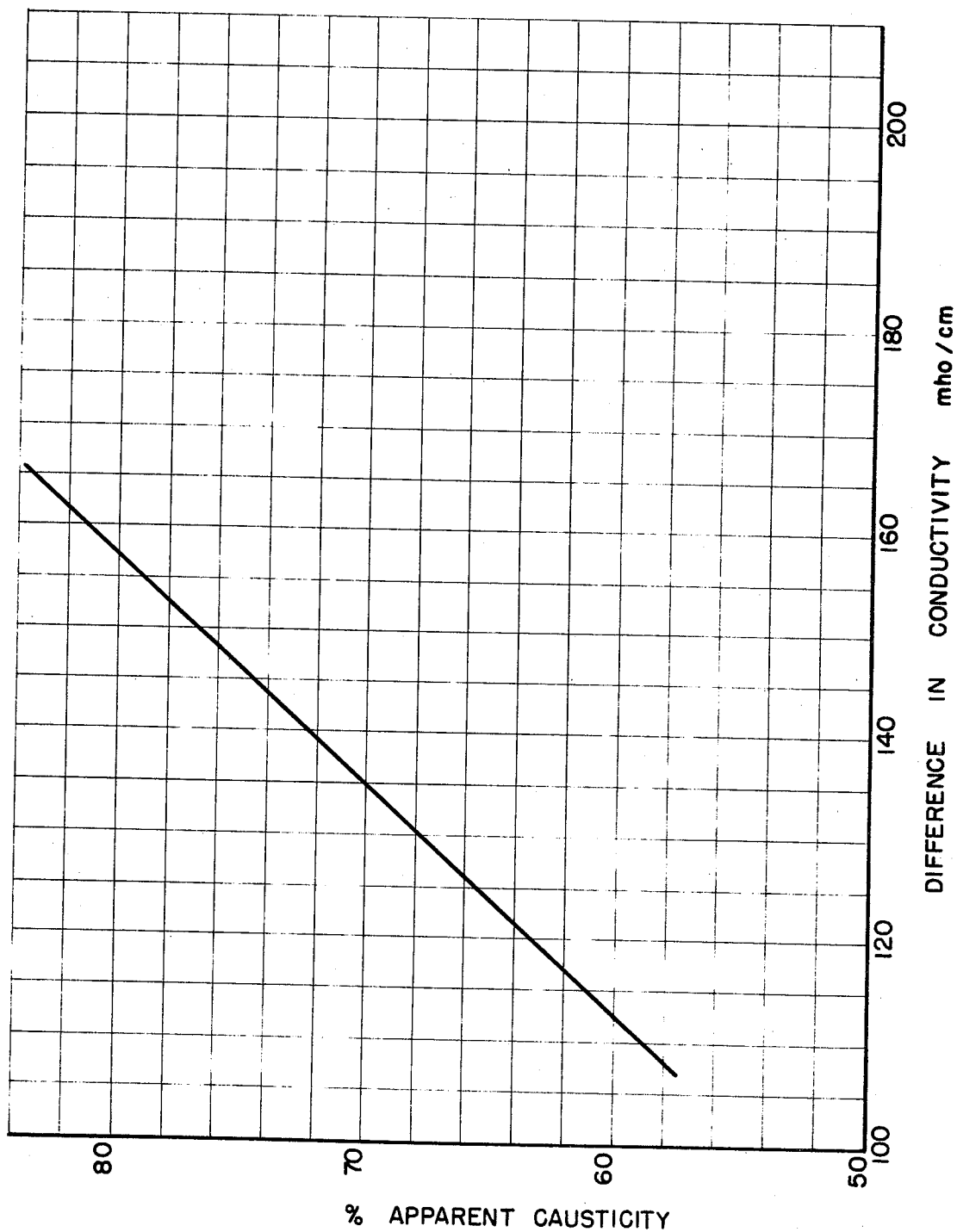**Anirudh K. Chowdhry**

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FIG. 2

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ANALYSIS OF KRAFT LIQUORS

BRIEF SUMMARY OF THE INVENTION

This invention relates to alkaline cooling liquors used in the manufacture of cellulosic pulp. More particularly, it relates to an effective and timely process for determining the apparent causticity of circulating kraft liquors which are used in the pulping of wood.

As is well known, one general method of preparing pulp, from which paper is made, is by cooking chips of wood in the presence of chemicals. In chemical pulping, the object is to selectively remove the lignious material in the wood chips and loosen cellulosic fibers so that when the pulping digester is blown, the fibers may be recovered. In the case of the kraft process, which is an alkaline cooking process, the primary cooking chemicals are sodium hydroxide and sodium sulfide, both of which are strong alkalies. These chemicals are contained in the cooking liquor, which at various stages of the kraft process is referred to as: white liquor, that which is charged to the digesters and having a high concentration of sodium hydroxide; black liquor, the spent liquor from the digesters; and green liquor, having a high concentration of sodium carbonate, prepared by dissolving recovered chemicals in water and weak liquor, from which white liquor is made by causticizing through the addition of lime.

With the development of chemical pulping processes has come the realization that better control over a cooking process is needed in order to obtain the most efficient use of the chemicals. The only controls exercised over most processes pertain to maintaining temperature and pressure over a period of time, and great reliance is usually placed on the experience of the operators to achieve a quality pulp. The need for monitoring a cooking liquor by quick and effective means has been recognized, and to some extent, met with a measure of success. It is, of course, possible to test in the laboratory a sample of liquor for apparent causticity, but this generally takes a half hour or more, and the time involved is much too long to allow for efficient corrections in the causticity of the liquor. Until the causticity of the liquor is corrected, inactive sodium carbonate, a byproduct formed during the smelting procedure of the well-known chemical recovery operation, is recycled to the digesters.

Analyzers have been proposed for determining the apparent alkalinity of a cooking liquor, but monitoring procedures proposed to date have used modification of normal analytical techniques and are therefore relatively slow by nature. In one proposed monitoring system, conductivity measurements are made before and after the liquor sample has been neutralized with carbon dioxide treatment, with the differential conductivity said to be proportional to the hydroxyl ion concentration of the liquor. This method is adequate for analyzing liquors having low concentrations of sodium hydroxide, as in black liquors, but when used to monitor a liquor having a high hydroxyl ion concentration, such as white liquor, the neutralizing time is prohibitively long for effective process control purposes. In another proposed system, changes in effective alkali are recorded as changes in percent light transmittance, the measurement being taken after the sample has been treated and passed through a cellulose membrane dialyzer.

The present invention is directed to a quick and effective method of determining the apparent causticity of kraft cooking liquors, regardless of the hydroxyl ion concentration of the liquor. According to the present invention, the soluble carbonates are quickly precipitated from the liquor by the addition of barium chloride, and it has been found that the difference between the conductivity of the liquor before and after the precipitation is directly proportional to the apparent causticity of the liquor. This property of the liquor can then be used to control necessary chemical additions to the circulating liquor in order to maintain an effective amount of cooking chemicals. Apparent causticity is defined as the amount of sodium hydroxide as sodium oxide, divided by the sum of the

amounts of sodium hydroxide, sodium sulfide, and sodium carbonate, all expressed as sodium oxide. Percent apparent causticity can be expressed according to the following:

Percent apparent causticity

$$= \frac{\text{NaOH as } Na_2O (g./l.) \times 100}{\text{NaOH} + Na_2S + Na_2CO_3, \text{ all as } Na_2O(g./l.)}$$

In practicing the present invention, a sample of kraft liquor is preferably filtered to remove any suspended materials, such as pulp particles and other debris likely to be found in cooking liquors. The conductivity of the liquor is then determined by using a standard conductivity cell. Barium chloride is then added to immediately precipitate the sodium carbonate in the liquor. The precipitated material is removed through filtering and the conductivity of the liquid is again determined. The difference between the conductivities before and after precipitation surprisingly has been found to have a straight line relationship with the apparent causticity of the liquor. The total time involved in obtaining the differential conductivity measurement according to the present invention need be no more than about 5 minutes.

Preferably the conductivity cell has a temperature compensator, as is available on some commercial conductivity measuring units, so that the temperature of the liquor has no influence on the conductivity measurements. If a conductivity cell, having no means for temperature compensation, is employed, the liquor is preferably cooled to a predetermined temperature before the conductivity measurements are made. The predetermined temperature is not critical, and cooling the liquor to about 25° C. has worked satisfactorily.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described with the aid of the following drawings, in which:

FIG. 1 is a simplified diagrammatic flow sheet of the process of this invention; and

FIG. 2 is a graph showing the relationship between the calculated percent apparent causticity of various kraft cooking liquors and differential conductivity measurements determined according to the present process.

DETAILED DESCRIPTION

Kraft cooking liquor is taken from the circulating cooking liquor of a kraft mill, as for example from the causticizer, passes through conduit 10 and is pumped by pump 12 through conduit 14, valve 16, to a self-cleaning filter 18 where fibers and other debris are removed from the liquor. The liquor then passes through conduit 20, cooling coil 22, where the temperature of the liquor is cooled to a predetermined temperature, such as 25° C., and then through conduit 24 to conductivity cell unit 26. It is obvious that if conductivity unit 26 is equipped with a temperature compensator, the cooling coil 22 may be eliminated and the liquid passed from filter 18 directly to conductivity unit 26. The electrical conductivity of the liquor is measured in unit 26 and a signal, corresponding to the value of the conductivity measurement, is sent to analog computer 28 via circuit 30.

When the above conductivity measurement is completed, valve 32 is opened and the liquor passes from unit 26 to vessel 34 by way of conduit 36. Simultaneously, a barium chloride solution (preferably about 10 percent by weight) is metered from supply tank 38, passing through valve 40 and conduit 42. The barium chloride solution is supplied to vessel 34 in an amount about equal to that of the liquor, on a volume basis. The soluble carbonates, especially sodium carbonate, immediately precipitate from the liquor which is then passed to self-cleaning filter 44 by means of pump 46, conduit 48, and valve 50. The precipitated materials are removed from the liquor by filter 44, and the liquor then passes into conductivity cell unit 26 by means of conduit 52. The electrical conductivity of the liquor is measured again and a second signal is sent via circuit 30 to analog computer 28 which performs, in known manner, a subtraction of the two conductivity mea-

surements. The differential conductivity is transmitted through line 54 to recorder 56 to provide a reading of the differential conductivity. When the differential conductivity determination is complete, the liquor is drained from the unit 26 by means of valve 58 and line 60.

To those skilled in the art, it will be readily apparent that analog computer 28 controls the various valve openings and closings by means of circuits 62, 64, 66, 68 and 70. Further, as will be understood, the conductivity cell unit 26 is standard and well known to those skilled in the art and may comprise, for example, a Beckman conductivity bridge arrangement, Model No. RD–16B2, including a Pyrex dip conductivity cell, Beckman Model No. CELBB1.

It is to be understood that FIG. 1 is diagrammatic of a flow pattern that may be utilized in practicing the present invention. Various changes may be made in the flow path. For example, filter 44 can be eliminated by routing conduit 48 back to filter 18. Obviously, the system is subject to other changes, as recognized by those skilled in the art.

The differential conductivity of a kraft cooking liquor, as determined according to the present process, has a straight line relationship with the apparent causticity of the liquor. Various samples of green and white kraft liquors were tested in the laboratory by a known analytical procedure for apparent causticity. This procedure involved dilution of a 5 ml. sample of liquor with water to 25 ml. The diluted liquor was then titrated with 0.322261 N HC1 to the phenolphthalein endpoint (A) and to the methyl orange endpoint (B). From the amounts of HC1 used for the two endpoints A and B, the apparent causticity was calculated as follows:

Percent apparent causticity =A—(B—A)/B ×100 The following data was obtained from the known analytical procedure for several kraft liquor samples:

Liquor No.	Percent Apparent Causticity
1	69.5
2	73.7
3	74.4
4	74.0
5	74.8
6	75.8
7	78.3
8	81.3

Differential conductivity measurements were determined for the above liquors according to the process of the present invention. Conductivity measurements were made after the samples were quickly cooled to about 25° C. The complete process took only about 4 minutes. The differential conductivities were as follows:

Liquor No.	Differential Conductivity (mho/cm.)
1	135.0
2	140.0

TABLE—Continued

Liquor No.	Differential Conductivity (mho/cm.)
3	145.0
4	144.0
5	146.0
6	147.0
7	153.5
8	161.0

A plot of the differential conductivities of liquors 1–8 against the calculated apparent causticities of the liquors obtained from the known analytical procedure is shown in FIG. 2.

From the above, it can be seen that the apparent causticity of kraft cooking liquors can be determined quickly and accurately according to the process of this invention. The speed of the process allows for timely corrections to be made in a kraft liquor so as to obtain the most efficient use of the kraft process and cooking chemicals.

It is obvious that variations may be made in the process of this invention without departing from the spirit and scope thereof.

I claim:

1. The process of determining the apparent causticity of an alkaline cooking liquor used in the pulping of wood which comprises the steps of:
   a. measuring the electrical conductivity of an alkaline cooking liquor;
   b. precipitating soluble carbonates from the cooking liquor;
   c. and measuring the electrical conductivity of the cooking liquor after the carbonates have precipitated,
   the difference between the conductivity measurements of steps (a) and (c) corresponding directly to the apparent causticity of the cooking liquor.

2. The process of claim 1 wherein the soluble carbonates are precipitated by the addition of barium chloride in solution to the alkaline cooking liquor.

3. The process of claim 1 which includes, before step (a), the step of cooling the cooking liquor to a temperature of about 25° C.

4. The process of determining the apparent causticity of a kraft cooking liquor used in the pulping of wood, wherein the liquor contains soluble carbonates, which comprises the steps of:
   a. filtering suspended materials from a kraft cooking liquor;
   b. passing the liquor through an electrical conductivity measuring device;
   c. measuring the electrical conductivity of the liquor for a first time;
   d. adding a solution of barium chloride to the liquid to precipitate the soluble carbonates in the liquor;
   e. filtering the precipitated carbonates from the liquor;
   f. passing the liquor through an electrical conductivity measuring device;
   g. and measuring the electrical conductivity of the liquor for a second time,
   the difference between the conductivity measurements of steps (c) and (g) corresponding directly to the apparent causticity of the cooking liquor.

5. The process of claim 4 which includes, between steps (a) and (b) the additional step of cooling the cooking liquor to a temperature of about 25° C.