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SYSTEM OF WOOD PULP DIGESTER CONTROL

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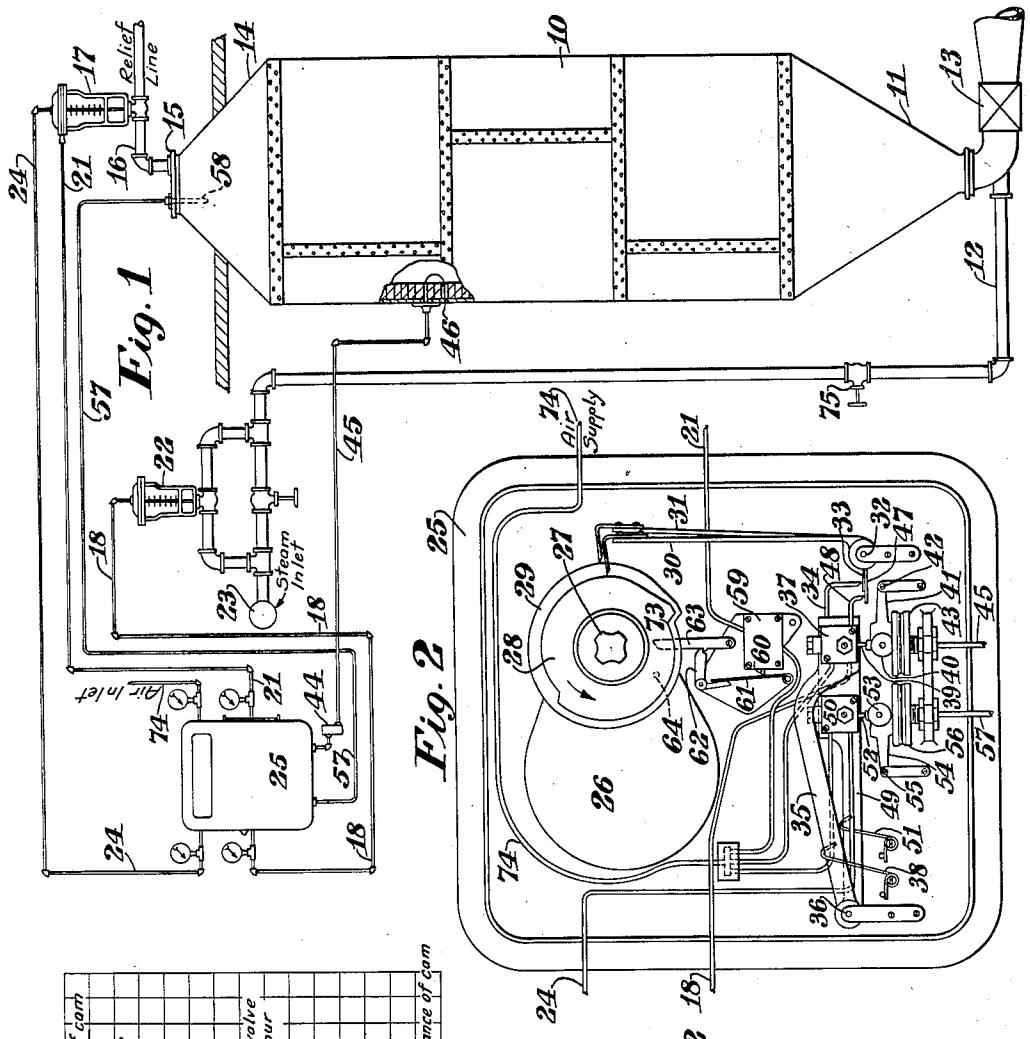


Fig. 1

Fig. 2

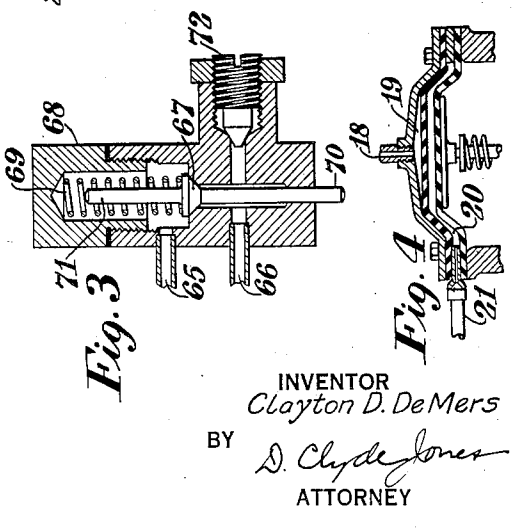


Fig. 3

Fig. 4

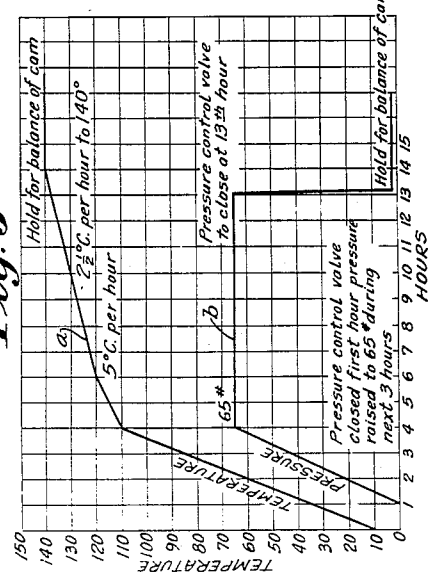


Fig. 5

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SYSTEM OF WOOD PULP DIGESTER CONTROL

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This invention relates to the automatic control of digesters such as are employed in the production of wood pulp.

In the manufacture of wood pulp according to the sulphite process, wherein wood chips are subjected to steam and chemical liquor including calcium and magnesium bisulphites in dilute sulphurous acid within a digester, it is essential that the temperature and pressure therein be carefully regulated according to prescribed schedules to the end that the maximum amount of wood pulp may be produced from a given quantity of wood stock with a minimum of precipitated insoluble salts, in order that the resulting wood fiber will be of superior quality.

It has been proposed many times in the past, to employed automatic regulation of the temperature and pressure within a digester of this type, but such proposed arrangements have never proved to be practical, probably due to the fact that it has not been possible to obtain an accurate determination of the temperature of the material in all parts of the digester. This difficulty arises from the fact that the wood chips and later, the resulting wood pulp, due to the structure thereof, are not adapted to circulate in the digester since it is not feasible to provide a mechanical agitator therein. Consequently, if a thermometer bulb is placed in the chemical or liquor charged with wood chips, there is danger that the chips will pack around the thermometer bulb thereby forming a pocket in which the temperature is not representative of the temperature in other parts of the material in the digester.

In order to overcome this difficulty, it has been proposed to employ a flow meter which definitely measures the amount of steam introduced into the body of the digester, but such an arrangement has not proved to be satisfactory, due to the fact that precipitated solids tend to form in the outlet of the digester and also in the relief line thereof, so that it is not only difficulty to discharge the digester but the pressure and temperature within the digester cannot be maintained at the prescribed values.

In accordance with the present invention, a novel system of regulation for a wood pulp digester is provided which overcomes the operating difficulties of prior devices and which maintains the temperature and pressure within the digester, according to a time-temperature and time-pressure schedule whereby a maximum yield of uniformly superior wood pulp results and whereby the time required to digest charges of wood are rendered more uniform.

Referring to the drawing, Fig. 1 represents a wood pulp digester and associated control mechanism for automatically controlling the temperature and pressure within the digester according to a predetermined schedule; Fig. 2 is a time-actuated pressure and temperature regulating instrument of a type suitable for use in the system of Fig. 1; Fig. 3 is a cross-section of a pilot air valve forming part of the control mechanism of Fig. 2; Fig. 4 is a cross-sectional view of the actuating top of a control valve suitable for use in the relief line of the digester; and Fig. 5 is a chart useful in explaining the invention and representing one schedule of related temperature and pressure which has been found to be effective in wood pulp digester control.

Referring especially to Fig. 1, 10 designates a wood pulp digester of any well-known construction formed of sheet steel lined with chemical-resisting material and having a conical bottom portion 11 into which live steam may be introduced through steam supply line 12 and through which the finished wood pulp may be blown into a receiving tank when the gate or valve 13 is opened. The upper part of the digester, which is in the form of a truncated cone 14, is provided with an opening at its top closed by the cap or crown 15. This cap 15 may be removed to charge the digester with uncooked wood chips and with chemical liquor (calcium and magnesium bisulphites in dilute sulphurous acid), after which it is clamped tightly in position by means (not shown).

With the digester thus charged with wood chips and liquor, the temperature and pressure within the digester should be closely regulated so that the maximum amount of pulp may be obtained from a given charge

of wood. In order to maintain the desired temperature within the digester, a relief line 16 communicates with the interior of the digester under the control of a fluid-actuated valve 17. This valve is herein shown as having two air-actuated diaphragms located in its top, one diaphragm being actuated by compressed air supplied through conduit 24 and the other being actuated by compressed air supplied through the conduit 21 which leads to a controlling instrument 25. The amount of steam introduced into the digester from the steam supply line through the pipe 12 is closely regulated by the valve 22, the setting of which is also controlled by compressed air supplied to its actuating top through the conduit 18. Conduit 24 in common with conduits 18 and 21 leads to the controlling instrument 25 which operates in a manner to be described, so that the temperature within the digester follows the time-temperature schedule represented by the graph "*a*" and the time-pressure schedule represented by the graph "*b*" of Fig. 5. In these graphs the ordinates represent temperature and pressure, while the abscissa represents time in hours.

The controlling instrument generally designated 25 includes clock mechanism 26 of any well-known construction which, through a well-known train of gears, drives the arbor 27 to turn the cams 28 and 29 counter-clockwise according to a predetermined time schedule. The edges of these cams, shaped in accordance with the predetermined control conditions as represented by graphs "*a*" and "*b*", are respectively engaged by the cam follower arms 30 and 31 which are pivotally mounted at 32 on the back of the instrument. The bell crank arm 47 of the follower 30 is engaged by the extension 48 on the movable arm 35. The arm which carries the pilot valve 37 is pivoted at 36 at the instrument back and is urged downward by the spring 38. The valve block 37, the structure of which will be hereinafter described, includes a valve of which only the valve stem 39 is shown in Fig. 2. This valve stem engages the surface of a cam member 40 which is carried by the arm 41 pivotally mounted on the back of the instrument at 42. The cam 40 rests on the upper surface of a capsular diaphragm or bellows 43 which communicates, through an oil seal 44, with a capillary 45 opening into the digester at 46 at such a position that it is normally below the surface of the liquor therein.

The follower arm 31 through its bell crank arm 33 engages the extension 34 carried by the pilot valve arm 49. This arm, which carries the pilot valve 50, is mounted on the common pivot 36 and is urged downward under the action of the spring 51. The valve stem 52 of the pilot valve 50 likewise engages the surface of a cam 53, which is carried by the cam arm 54 pivotally supported at 55. The cam 53 rests on the upper surface of the capsular diaphragm or bellows 56 which communicates through the capillary system 57 to a temperature-sensitive bulb 58 mounted to extend into the space above the liquor when the digester is charged. As herein shown, this temperature-sensitive bulb is mounted in the cap 15 of the digester. There is also supported on the back of the instrument, a pilot valve block 59 including a valve of which only the stem 60 is shown in this figure. As herein illustrated the valve stem 60 is held in its innermost position by the pivoted arm 61 so that the valve in this block is open. This arm is normally held in the position shown by the latch 62 by engagement with a projection on the pivoted trigger arm 63. The trigger arm is actuated by a pin 64 carried on the cam 29 so that in the counter-clockwise movement of the cam, the trigger arm is moved to the right to disengage the latch 62. This releases the arm 61 permitting it to move to the left so that the valve within the block 59 can close.

While the structure of the valve blocks in this disclosure are well known, there is illustrated in the enlarged cross section of Fig. 3, a pilot valve suitable for use in this system. The block 68 includes the inlet port 65 and the outlet port 66 with the fluid passage between these ports controlled by the valve disk 67 engaging the valve seat within the valve block. The valve disc is carried by the valve stem 70 and the valve disc is arranged to be forced into its closed position by a spring 69 surrounding the extension 71 of the valve stem. In the side of the valve block there is provided a set screw 72 which serves as an adjustable leak functioning in the well-known manner to control the operation of the valve.

In the operation of the system the cap 15 is removed and the digester is charged through its open top with wood chips of uniform size and with liquor consisting of a solution of calcium and magnesium bisulphites in dilute sulphurous acid. The amount of this liquor is such that it covers the wood chips and leaves but a small free space in the top of the digester. When the cap 15 has been tightly clamped in the position shown, the hand valve 75 in the steam supply line 12 is then opened and in accordance with the control herein provided, the valve 17 in the relief line is closed. It is assumed that the clock 26 has been started and that the cams 28 and 29 have been set at the "starting point" herein indicated at 73. As these cams rotate counter-clockwise, the cam followers 30 and 31 are actuated in accordance with the contour of cams 28 and 29, respectively. However, since the pilot valve 59 is normally locked open by reason of the arm 61 holding its valve stem 60 depressed,

the compressed air from the air supply 74 is applied through the conduit 21 to hold the valve 17 closed since the pilot valve 50 is ineffective to control the valve 17 in response to the temperature-sensitive element 58 until such time as the pin 64 disengages the trigger arm 63. During such time as the follower arm 30 is engaging the contour of the cam 28, the bell crank arm 47 through extension 48 correspondingly raises and lowers the pilot valve arm 35 to vary the position of the pilot valve block 37 and therefore the setting of its valve, so that desired pressures are maintained within the digester according to the predetermined schedule represented by graph "*b*". It will be understood that as the pressure within the digester varies, this pressure applied through the capillary 45 and oil seal 44 expands or contracts the capsular diaphragm 43 which, through the action of cam 40 and valve stem 39, varies the opening in the valve block 37. In this manner the valve therein responds to changes in pressure within the digester to permit more or less compressed air to pass from the supply line 74 to the conduit 18 leading to the actuating top of the valve 22 in the steam supply line. It will be appreciated that as the pressure drops within the digester, the valve 22 is actuated in the manner just described to admit more steam and therefore increase the pressure therein.

It has been pointed out that the valve in the valve block 59 permits the application of compressed air to the top of the valve 17 in the relief line, so that this valve is held closed until such time as the pin 64 releases the trigger 63, thereby permitting the valve in block 59 to close. After this takes place, the temperature-sensitive element 58 in the top of the digester is effective through the capillary 57 and the capsular diaphragm 56 to control the operation of the pilot valve 50, so that from this point in the cook the temperature within the digester is controlled according to a definite schedule, represented by graph "*a*" in accordance with the cutting of the cam 29. It will be understood that when the temperature within the digester drops below the desired value as determined by the cam 29, the valve 17 in the relief line is opened in accordance with the well-known throttling action of a fluid-pressure operated valve to lower the pressure within the digester. As soon as the pressure therein drops, the pilot valve 39 is operated in response to this pressure change to apply compressed air to the actuating top of steam valve 22. Valve 22 thus admits steam into the digester through pipe 12 to restore the desired pressure, and consequently the temperature of the mass therein.

It is essential during the first stages of the process, that the liquor penetrate completely and uniformly into the wood chips in order that the chemical action taking place may be uniform throughout the mass. In this way none of the wood chips will be overcooked or undercooked. This peneration of the liquor into the chips is accelerated by pressure and as indicated in graph "*b*", the pressure should rise gradually for a relatively long period, for example, four hours, after which the pressure should be maintained uniform for the remainder of the period up to the thirteenth hour. Thereafter the pressure should be greatly reduced and then held at the greatly reduced pressure until the end of the cook. This entire pressure schedule is maintained under the control of pressure cam 28. The chemical action which takes place within the digester, is also dependent to a considerable extent on the temperature maintained in the digester, this action taking place at a more rapid rate in the presence of high temperature. Therefore, the temperature schedule indicated by graph "*a*" of Fig. 5 should be maintained within the digester, the later portion of this cycle being maintained under the control of the temperature cam 29.

Thus, in the preliminary stages of the cook, it is desirable to raise the pressure slowly and at the same time maintain a relatively low temperature. As the cooking period progresses, the chemical action may be accelerated by raising the temperature after the initial penetration of the liquid. This reaction is also effected by the acid concentration taking place more rapidly, as the amount of free sulphur dioxide is increased. Thus, after the preliminary cooking period and after the pressure has arrived at a value that insures through penetration, the temperature may be raised to accelerate the chemical reaction of the cooking process and to aid in the recovery of the sulphur dioxide from the acid solution.

For purposes of this description, the temperature in the digester may be attributed solely to the heat added by the steam of the cooking process. However, the pressure within the digester is determined first by the condensed steam; second, by the increased temperature of the gas above the liquid; third, by the gas expelled from the liquid by the steam; fourth, by the sulphur dioxide gas reaching the top surface of the liquid; fifth, by the increased volume of the liquid and solid contents of the digester due to an increased temperature and volumetric changes in the capacity of the digester caused by temperature rises in the lining thereof which do not exist in its steel shell. The condensed steam increases the total quantity of liquor and by decreasing the volume of the gas causes an increase in pressure.

The influence of the sulphur dioxide in effecting the pressure is relatively complex, but its action is believed to be as follows although the invention is not limited by this theory:

Since the steam is admitted at the bottom of the digester, that portion of the liquid immediately in contact with the steam has its sulphur dioxide expelled because the existing pressure within the digester is not sufficient to maintain it in the liquid at the temperature of the condensed steam. This liberated sulphur dioxide rises through the mass in the digester at a greater rate than the heated liquid at the steam inlet and is carried to the top by thermal convection. The sulphur dioxide therefore starts on its journey to the top of the digester at a high temperature and with considerable volume, but before arriving at the top must pass through cooler masses of material and may be either totally absorbed, or partially absorbed and partially liberated at the top of the mass. If it is absorbed the pressure increase caused by it, decreases during the absorption process, and no permanent pressure increase results. If it is only partially absorbed and arrives at the free surface of the liquid, it mixes with the gas above the liquid to give a permanent increase in the digester pressure.

In general, a column of warm liquid will be established from the steam inlet of the digester to the top thereof by thermal convection currents which cause the cooler liquid to descend toward the bottom along the lining of the digester. It is through this warm central column of liquid that the sulphur dioxide will rise to be liberated as free gas with a temperature above that of the liquid.

From the above description of the process of pressure change, it can be seen that any pressure may be attained, depending on the steam supply pressure, but because of the presence of gas above the liquid the temperature at that pressure will not be the temperature of saturated steam. For any definite pressure there will exist a corresponding maximum temperature. After the digester has been raised to the desired pressure during the initial cooking operations, no further increase in temperature can be effected, except by the admission of steam with the simultaneous release of a portion of the gas above the liquid.

By operating the relief valve 17 in the relief line 16 at the top of the digester, the temperature within may be raised to that of saturated steam at any pressure which it is desirable to maintain, if steam is admitted at such a rate that the pressure remains constant. A rise in temperature within the digester is effected as follows: When the relief valve 17 is opened the compressed gases above the liquid will tend to escape and the pressure within the digester will fall. Assuming that the pressure is maintained constant by the air-actuated valve 22 in the steam inlet line under the control of regulator 25, it is possible to add heat units to the digester by regulating the opening of the relief line 16. A thoroughly accurate measure of the temperature within the digester can now be secured under the control of the temperature-sensitive element 58 placed in the atmosphere above the liquid. The indication of this temperature element will give an average temperature of the digester because when the pressure within the digester falls, the sulphur dioxide contained in the liquid is released from all portions within the digester, since all portions thereof are at the same pressure. Each element of gas in rising to the top of the digester carries with it the average temperature of the liquid through which it has traveled. The mixing of all of these elements of gas above the liquid gives a very fair average temperature for all portions of the digester. Accordingly, the temperature within the digester may be controlled by maintaining the pressure at a definite value and by opening or closing the relief line accordingly as the temperature is below or above that which it is desired to obtain.

While the system herein disclosed makes use of compressed air or fluid actuated valves, the invention is not so limited. It will be understood, however, that various types of valves and various arrangements for regulating them, may be employed to control the temperature and pressure within a digester according to predetermined schedules, without departing from the spirit of the present invention.

I claim:

1. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a valve therein, a heating medium supply line communicating with said chamber, said supply line having a valve therein, a temperature-sensitive element and a pressure-sensitive element each being responsive to conditions within said chamber, and means including a time-actuated device cooperating with said temperature and pressure elements serving to regulate said valves whereby related predetermined schedules of pressure and temperature are maintained within said digester.

2. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a heating medium supply line communicating with the bottom of said chamber, a pressure fluid actuated valve in said relief line, a pressure fluid actuated valve in said supply line, a temperature-responsive element and a pressure responsive element, each having a portion extending into said chamber, and means including a time-actuated device cooperating with said temperature and pressure responsive elements serving to apply fluid pressure to said valves for maintaining related predetermined schedules of pressure and temperature within said digester.

3. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a valve therein, a steam supply line communicating with said chamber, said steam supply line having a valve therein, a temperature-sensitive element and a pressure-sensitive element, each being responsive to conditions within said chamber, said temperature-sensitive element being responsive to the temperature of the gaseous space in said chamber when said digester is in operation, and means including a time-actuated device cooperating with said temperature and pressure-responsive elements serving to regulate said valves whereby predetermined schedules of pressure and temperature are maintained within the digester.

4. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with the bottom of said chamber, a pressure fluid actuated valve in said steam line, a temperature-responsive element having a portion thereof extending into the gaseous space in said chamber when said digester is in operation, a pressure-responsive element having a portion thereof communicating with that part of the chamber that is filled with liquid when the digester is in operation, and means including a time-actuated device cooperating with said temperature and pressure responsive elements, serving to apply fluid pressure to said valves for maintaining related predetermined schedules of pressure and temperature within said digester.

5. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a relief valve therein, a steam supply line communicating with said chamber, said steam supply line having a regulating valve therein, a thermo-sensitive element and a pressure-sensitive element responsive to conditions within said chamber, and means for maintaining predetermined related schedules of temperature and pressure in said chamber, said means including a time-actuated device and said thermo-sensitive element for actuating said relief valve and including said time-actuated device and said pressure-sensitive element for actuating said supply valve.

6. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with the bottom of said chamber, and time cycle means for maintaining a predetermined schedule of pressure and a related predetermined schedule of temperature within said digester, said means comprising mechanism responsive to temperature for lowering the pressure within said digester and mechanism responsive to pressure within the digester for restoring the predetermined pressure therein.

7. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber and a steam supply line communicating with the bottom of said chamber, a valve in said relief line, a valve in said steam supply line, means including said valves for maintaining the pressure within said digester according to a predetermined schedule for a given period, said means including mechanism for maintaining said relief valve closed for a predetermined portion of said period and then for the remainder of said period serving to operate said valves in order to maintain a predetermined schedule of temperature in said digester.

8. In a system of digester control, a digester having a chamber therein, a relief line including a relief valve communicating with said chamber, said relief valve having two actuating diaphragms, a steam supply line including a supply valve communicating with said chamber, a thermo-sensitive element including means responsive to the temperature within said chamber, a pressure element provided with means responsive to pressure within said chamber, means including a time-actuated mechanism and said pressure-responsive device for regulating said supply valve to maintain a predetermined schedule of pressures in said chamber during a given period, means for supplying pressure fluid to one actuating diaphragm of said relief valve during a predetermined period to hold said relief valve closed, and means including said time-actuated device for thereafter supplying fluid pressure to the second diaphragm of said relief valve to regulate same in accordance with temperature.

9. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with the bottom of said chamber, and a time cycle device for maintaining a predetermined schedule of pressure and a related predetermined schedule of temperature within said digester, said device comprising means responsive to temperature for lowering the pressure within said digester and means responsive to pressure within the digester for restoring the predetermined pressure therein.

10. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a valve therein, a pressure supply line communicating with said chamber, said supply line having a valve therein, a temperature-sensitive element and a pressure-sensitive element each being responsive to conditions within said chamber, and means including a time-actuated device cooperating with said temperature and pressure elements

serving to regulate said valves whereby related but independently regulated predetermined schedules of pressure and temperature are maintained within said digester.

11. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with the bottom of said chamber, a pressure-fluid actuated valve in said relief line, a pressure-fluid actuated valve in said steam line, a temperature-responsive element and a pressure-responsive element, each having a portion extending into said chamber, and mechanism including time-actuated means cooperating with said temperature and pressure-responsive elements serving to supply fluid pressure to said valves for maintaining variable but independently regulated predetermined schedules of pressure and temperature within said digester.

12. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a valve therein, a steam supply line communicating with said chamber, said steam supply line having a valve therein, a temperature-sensitive element and a pressure-sensitive element, each being responsive to conditions within said chamber, said temperature-sensitive element being responsive to the temperature of the gaseous space in said chamber when said digester is in operation, and mechanism including time-actuated means cooperating with said temperature and pressure-responsive elements serving to regulate said valves whereby predetermined schedules of pressure and temperature are maintained within the digester.

13. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, said relief line having a pressure-fluid actuated valve therein, a steam supply line communicating with the bottom of said chamber, a pressure-fluid actuated valve in said steam line, a temperature-responsive element having a portion thereof extending into the gaseous space in said chamber when said digester is in operation, a pressure-responsive element having a portion thereof communicating with that part of the chamber that is filled with liquid when the digester is in operation, and mechanism including time-actuated means cooperating with said temperature and pressure-responsive elements, serving to apply fluid pressure to said valves for obtaining separately maintained predetermined schedules of pressure and temperature within said digester.

14. In a system of digester control, a digester having a chamber therein, a relief line communicating with said chamber, said relief line having a relief valve therein, a steam supply line communicating with said chamber, said steam supply line having a regulating supply valve therein, a thermo-sensitive element and a pressure-sensitive element responsive to conditions within said chamber, and mechanism for maintaining predetermined related schedules of temperature and pressure in said chamber, said mechanism including time-actuated means and said thermo-sensitive element for actuating said relief valve and including said time-actuated means and said pressure-sensitive element for actuating said supply valve.

15. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with the bottom of said chamber, and time cycle mechanism for maintaining a predetermined schedule of pressure and a related predetermined schedule of temperature within said digester, said mechanism comprising means responsive to temperature for lowering the pressure within said digester, and means responsive to pressure within the digester for restoring the predetermined pressure therein.

16. In a system of digester control, a digester having a chamber therein, a relief line including a relief valve communicating with said chamber, said relief valve having two actuating diaphragms, a steam supply line including a supply valve communicating with said chamber, a thermo-sensitive element including means responsive to the temperature within said chamber, a pressure element provided with means responsive to pressure within said chamber, means including time-actuated mechanism and said pressure-responsive device for regulating said supply valve to maintain a predetermined schedule of pressure in said chamber during a given period, means for supplying pressure fluid to one actuating diaphragm of said relief valve during a predetermined period to hold said relief valve closed, and means including time-actuated mechanism for thereafter supplying fluid pressure to the second diaphragm of said relief valve to regulate same in accordance with temperature.

17. The method of maintaining a desired schedule of pressures and a desired schedule of temperatures in a pulp digester which comprises changing the pressure in the digester in response to desired changes in temperature and introducing steam into said digester in response to the change in pressure to restore the desired schedule of pressure therein.

18. The method of maintaining a desired variable schedule of pressures and a desired differently variable schedule of temperatures within a pulp digester which comprises changing the pressure in the digester in response to a change of temperature therein and in accordance with a predetermined

temperature schedule, and introducing a heating medium under pressure into said digester in response to a change in pressure therein and in accordance with a predetermined schedule of pressures.

19. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, a steam supply line communicating with said chamber, and time cycle mechanism for controlling the operation of said digester according to schedule, said mechanism comprising means operating according to a schedule for relieving the pressure within said digester through said relief line and means responsive to pressure within said digester for restoring a predetermined pressure schedule therein, through said supply line.

20. The method of maintaining a desired schedule of conditions in a pulp digester, which comprises relieving the pressure in the digester according to a predetermined schedule, and introducing steam into said digester in response to the changes in pressure to restore a predetermined schedule of pressures therein.

21. In a system of digester control, a digester having a chamber therein, a relief line communicating with the top of said chamber, said relief line having a pressure-fluid actuated valve therein, a steam supply line communicating with said chamber, a pressure-fluid actuated valve in said steam line, a pressure-responsive device having a portion thereof communicating with the interior of said chamber, mechanism including time-actuated means functioning to apply pressure fluid to the valve in the relief line to open the same according to schedule, and means including said time-actuated means and said pressure-responsive device for supplying pressure fluid to the valve in the steam supply line to open the same so that a predetermined schedule of pressure is maintained within said digester.

In testimony whereof I affix my signature.

CLAYTON D. DE MERS.