April 12, 1932. T. T. GRAY 1,853,972

REFINING HYDROCARBONS

Filed Aug. 9, 1926 2 Sheets-Sheet 1

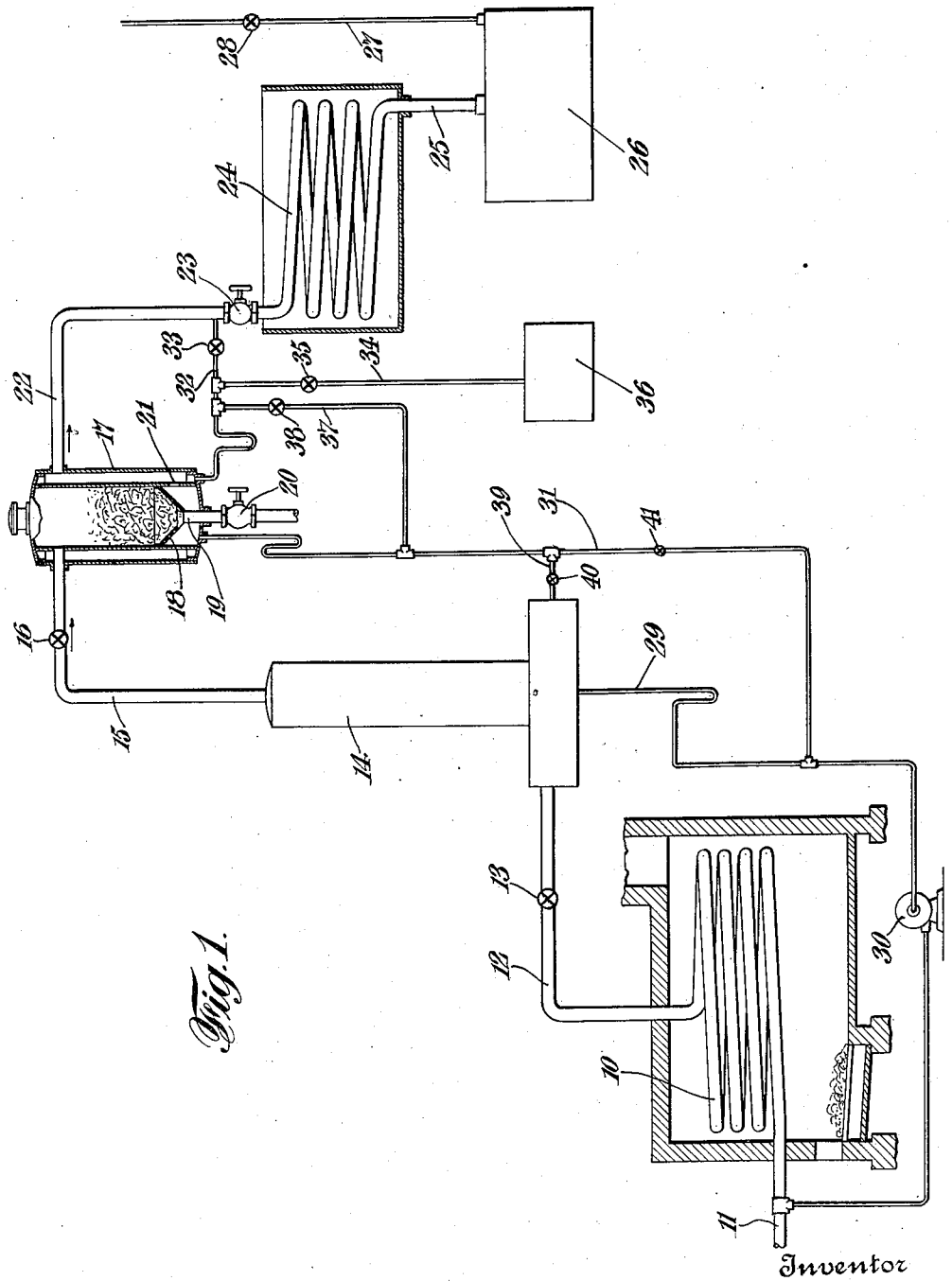

Fig. 1.

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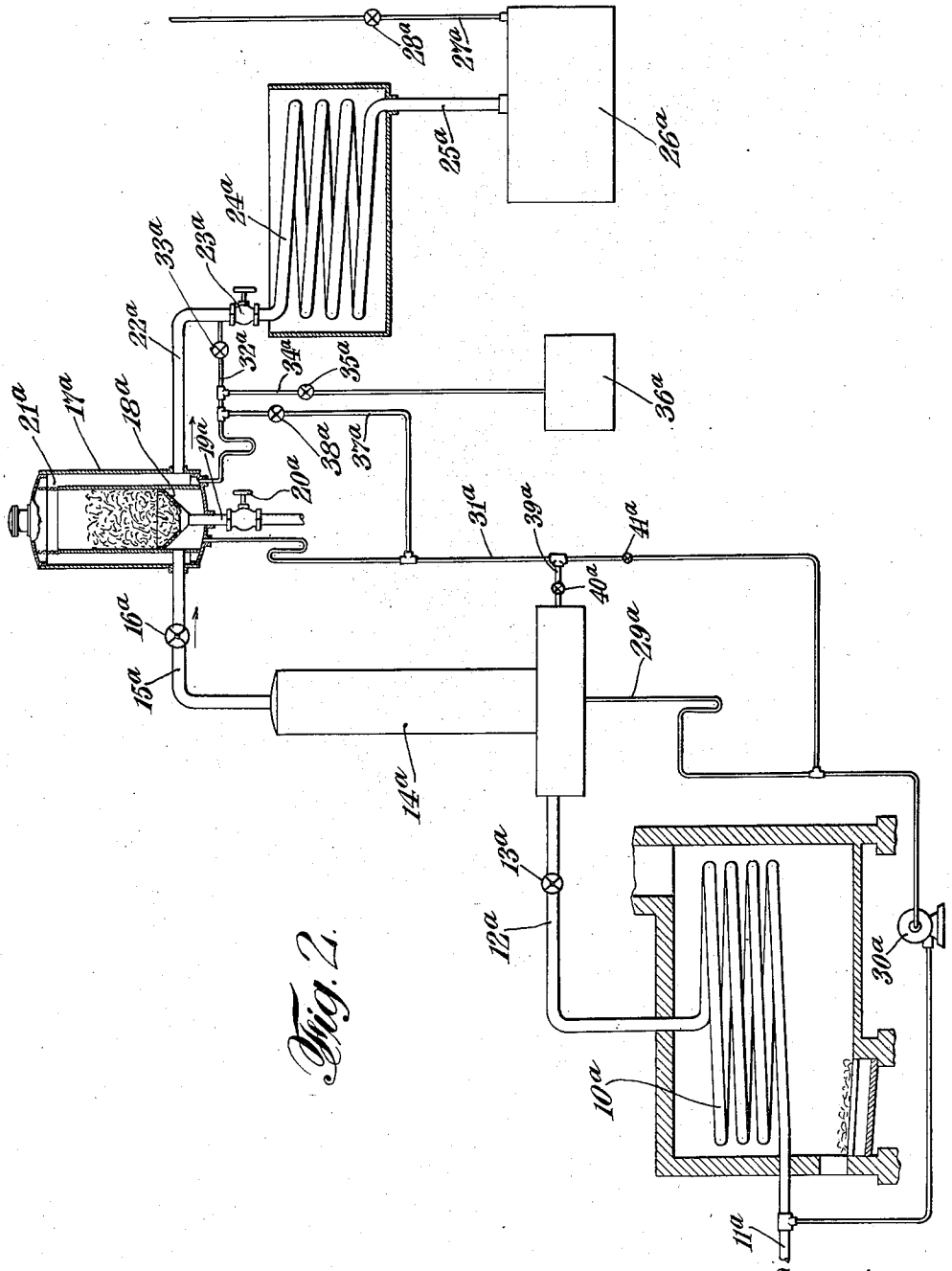

Fig. 2.

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Patented Apr. 12, 1932 1,853,972

UNITED STATES PATENT OFFICE

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REFINING HYDROCARBONS

Application filed August 9, 1926. Serial No. 128,008.

This invention relates to the refining of hydrocarbons and more especially to the refining of cracked distillate by the polymerization and removal of unstable hydrocarbons which render them unsuitable for use as motor fuel.

Cracked petroleum distillates contain unstable unsaturated hydrocarbons which are polymerized on standing thereby impairing the quality of gasolene. In applicant's Patent No. 1,340,889 there is disclosed a process for polymerizing and removing the undesirable hydrocarbon compounds of cracked distillate which consists in bringing the cracked distillate in vapor form into contact with a catalytic agent such for example as fuller's earth. To prevent excessive loss of the desired product by condensation of vapor in the treating material, the latter is best maintained substantially at the temperature of the vapors.

An object of the invention is to derive heat from the treated vapor to maintain the temperature of the treating material substantially the same as that of the vapor to be treated.

According to the invention the treating material is contained within a chamber surrounded by an annular space. The vapor to be treated is introduced into the chamber and caused to contact with the treating material thereby polymerizing the unstable unsaturated hydrocarbons in the vapor. The polymers thus formed are drained from the treating material and collected together with the condensate resulting from the condensation in the treating material of any of the vapor. The polymers and condensate may be refluxed into the system for redistillation. The treated vapor is then conducted into the annular chamber and circulated about the container, thereby establishing a heat exchange relationship between the vapor and the treating material. The vapor acts as an insulating blanket around the treating material and minimizes radiation losses so that the treating material is maintained substantially at the temperature of the vapor being treated. Some of the treated vapor is condensed in the annular chamber and because of the fact that the undesirable hydrocarbons have been polymerized and removed prior to its condensation, the condensate may be conducted directly to the condenser in which the vapor issuing from the annular chamber is condensed.

Other objects, novel features and advantages of the invention will be apparent from the following specification and accompanying drawings wherein

Figure 1 discloses one form of apparatus for treating cracked distillates in accordance with the invention, and

Figure 2 discloses a modified form of apparatus.

10 designates a still of the tube type to which oil to be cracked or a cracked distillate from a previous cracking operation is supplied from a source not shown through a pipe 11. The still is connected through a pipe 12 controlled by a valve 13 with a fractionator 14 which is of any suitable type and capable of producing the desired fraction which may be gasoline of definite boiling range. From the fractionator a pipe 15 controlled by the valve 16 leads to a treating tower 17. This tower comprises an inner and an outer shell arranged to form a central chamber and an annular surrounding chamber. Within the central chamber is provided a funnel-shaped perforated shelf 18 terminating in a discharge spout 19 leading through the bottom of the treating tower and controlled by a valve 20. Below the shelf 18 there is provided an aperture 21 in the inner shell of the tower 17 through which communication is established between the inner and outer chamber. The pipe 16 extends through the annular chamber and communicates only with the central chamber at a point above the shelf 18. A

pipe 22 controlled by a valve 23 communicates with the upper end of the annular chamber and leads to a condenser 24. From the condenser a pipe 25 leads to a receiving tank 26 which is provided with a vent pipe 27 controlled by a valve 28. A reflux pipe 29 leads from the fractionator 14 to the supply line 11 for the still 10. A reflux pipe 31 leads from the central chamber of the tower 17 to the pipe 29. A trapped pipe 32 controlled by valve 33 leads from the bottom of the annular chamber of the tower 17 to the pipe 22 at a point ahead of the valve 23. A pipe 34 controlled by a valve 35 leads from the pipe 32 at a point ahead of the valve 33 to a storage tank 36. A pipe 37 controlled by valve 38 leads from the pipe 32 at a point ahead of the valve 33 to the reflux pipe 31. A pipe 39 controlled by a valve 40 leads from the pipe 31 to the base of the fractionating tower 14 and a valve 41 is provided in the pipe 31 below the pipe 39. By proper manipulation of the valves 40 and 41, any liquid collecting in the bottom of the central chamber of tower 17 may be refluxed either to the fractionator 14 or the still 10. Also by regulation of the valves 33, 35, 38, 40 and 41, any liquid collecting in the annular chamber of tower 17 may be caused to flow as desired into the condenser 24, the tank 36 or the pipe 31 through which it may be refluxed directly to the still 10 or to the fractionator 14. The outer surface of the tower may, if desired, be provided with a layer of heat insulating material. By means of the valves 13, 16, 23, 28, the pressure in different portions of the system may be regulated as desired. Vapor from the fractionator may be supplied to the treating tower under atmospheric or superatmospheric pressure by proper regulation of the valves.

In Fig. 2, 10*a* is the still to which oil is supplied through pipe 11*a*. From the still a pipe 12*a* controlled by a valve 13*a* leads to a fractionator 14*a* which may be of any suitable type to yield the desired fraction which may be gasoline of definte boiling range. A pipe 15*a* controlled by a valve 16*a* leads to a treating tower 17*a*. The treating tower comprises an inner and an outer shell dividing the tower into a central and an annular chamber. The upper portion of the inner shell is formed of screening or netting 21*a* thereby establishing communication between the inner and outer chambers. Within the inner shell is provided a funnel-shaped perforated shelf 18*a* terminating in a discharge spout 19*a* extending through the bottom of the tower and controlled by a valve 20*a*. The pipe 15*a* extends through the annular chamber and communicates only with the central chamber at a point below the shelf 18*a*. A pipe 22*a* controlled by a valve 23*a* communicates with the annular chamber at a point near the bottom thereof and leads to a condenser 24*a*. From the condenser a pipe 25*a* leads to a storage tank 26*a* provided with a vent pipe 27*a* controlled by a valve 28*a*. A reflux line 29*a* leads from the fractionator 14*a* through a pump 30*a* to the supply pipe 11*a* for the still 10*a*. A reflux line 31*a* leads from the bottom of the central chamber of the tower 17*a* to the pipe 29*a*. A pipe 32*a* controlled by a valve 33*a* leads from the bottom of the annular chamber of the tower 17*a* through a trap to the pipe 22*a*. A pipe 34*a* controlled by a valve 35*a* leads from the pipe 32*a* at a point ahead of the valve 33*a* to a tank 36*a*. A pipe 37*a* controlled by a valve 38*a* leads from the pipe 32*a* at a point ahead of the valve 33*a* to the pipe 31*a*. A pipe 39*a* controlled by a valve 40*a* leads from the pipe 31*a* to the base of the fractionating tower 14*a* and a valve 41*a* is provided in the pipe 31*a* below the pipe 39*a*. By proper manipulation of the valves 40*a* and 41*a*, any liquid collecting in the bottom of the central chamber of tower 17*a* may be refluxed either to the fractionator 14*a* or the still 10*a*. Also by regulation of the valves 33*a*, 35*a*, 38*a*, 40*a* and 41*a*, any liquid collecting in the annular chamber of tower 17*a* may be caused to flow as desired into the condenser 24*a*, the tank 36*a* or the pipe 31*a* through which it may be refluxed directly to the still 10*a* or to the fractionator 14*a*. The pressure in the different parts of the system may be regulated by means of the valves 13*a*, 16*a*, 23*a* and 28*a*.

The inner chamber of the treating tower in each apparatus is charged with a material capable of polymerizing the undesirable unsaturated hydrocarbons present in cracked distillate. This material is prevented from sifting through the perforations in the shelf by means of screens or layers of mineral wool or the like.

In the operation of the apparatus disclosed in Fig. 1 the still 10 is heated and oil to be cracked or a previously cracked distillate is admitted thereto. The distillate is supplied to the fractionator from which is discharged the desired fraction which may be gasoline of definite boiling range. The vapor from the fractionator is led into the upper part of the central chamber and caused to flow downwardly through the treating material. During the flow of the vapor through the treating material the undesirable unsaturated hydrocarbons are polymerized. The polymers thus formed being of higher boiling point than the temperature of the vapor become liquid and drip through the perforations into the bottom of the inner chamber. The treated vapors escape through the aperture 21 into the annular chamber and are led up around the inner shell thereby being brought into heat exchange relation with the heating material. The treating material is thus maintained at a sufficiently high temperature to prevent excessive condensation of vapor

during the polymerizing operation. Some of the vapor is cooled in this operation and condensed. This condensate is led out through the pipe 32 either to the condenser 24 or storage tank 36 or is refluxed through the pipe 37 for redistillation as desired. The polymers together with any condensate that may have been formed in the polymerizing operation may be refluxed into the still or into the fractionator 14.

The operation of the apparatus disclosed in Fig. 2 is substantially the same as the apparatus disclosed in Fig. 1. In this apparatus the vapor to be treated flows upwardly through the treating material instead of downwardly as in the apparatus of Fig. 1.

In each modification treated vapor is caused to circulate around the container to the treating material at a temperature substantially that of the vapor to be treated. In each instance the liquid collecting in the annular chamber has been condensed from treated vapor and constitutes part of the desired product. It may, therefore, be taken directly to the condenser and there mixed with the condensate from the vapor discharged from the tower. The valves in the vapor line may be adjusted to attain the pressures desired in the different parts of the system so that if desired the vapor to be treated may be brought into contact with the treating material either at atmospheric or super-atmospheric pressure.

The treating material is thus maintained at an effective temperature without any loss of efficiency in the operation of the system after the treating material has once become thoroughly heated. The condensate collecting in the annular chamber comes from vapor which has been subjected to the treating material and is therefore a part of the finished product. Of course some of the desired product may be condensed in the treating material and collected with the polymers in the lower portion of the annular chamber of the treating tower. This condensate together with the polymers may be refluxed for redistillation. Such condensate may at the beginning of the operation be considerable because of the fact that the treating material has not been brought up to temperature but after the treating material has been brought up to temperature, such condensate is comparatively small.

The treating material, where it is desired simply to remove the unstable unsaturated hydrocarbons from the vapors, may be fuller's earth, bauxite, or any other adsorbent substance. Where it is also desired to remove sulfur compounds the agent may be a metal or metallic compound having an affinity for the sulfur compounds in the vapors, which may be mixed with an adsorbent material.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of obtaining motor fuel from petroleum which comprises distilling petroleum under super-atmospheric pressure, passing the vapor of distillation while under superatmospheric pressure through a body of solid treating material capable of polymerizing the unstable, unsaturated hydrocarbons present in the vapor, draining from said treating material condensate comprising polymers formed in the treating material, withdrawing the treated vapor from the treating material and passing the same into indirect heat exchange relation with the treating material to reduce loss of heat from the treating material by radiation and subsequently condensing the vapor.

2. The method of refining petroleum products containing unstable, unsaturated compounds which consists in passing the same in vapor phase through a body of solid treating material capable of polymerizing said unstable, unsaturated compounds, withdrawing from the body of treating material condensate comprising polymers formed therein, withdrawing treated vapor from said treating material and passing the same into indirect heat exchange relation therewith to reduce loss of heat from the treating material by radiation and subsequently condensing said vapor.

3. The method of refining cracked petroleum products which comprises passing the same in vapor phase and under super-atmospheric pressure through a body of solid treating material capable of polymerizing the unstable, unsaturated hydrocarbons present in said vapor, draining from said body of treating material condensate including polymers formed therein, withdrawing the treated vapor from said body of treating material and passing the same into indirect heat exchange relation therewith to reduce loss of heat from the treating material by radiation and subsequently condensing the vapor.

4. The method of refining cracked petroleum products which comprises passing the same in vapor form through a body of solid treating material capable of polymerizing the unstable, unsaturated compounds contained in the vapor, draining from said body of treating material condensate comprising polymers formed therein, separating the treated vapor from said condensate, passing said treated vapor into indirect heat exchange relation with said treating material to reduce loss of heat from the treating material by radiation and subsequently condensing the treated vapor.

5. The method of refining cracked petroleum products which comprises passing the same in vapor form and under super-atmospheric pressure through a body of solid treat-

ing material capable of polymerizing the unstable, unsaturated compounds contained in the vapor, draining from said body of treating material condensate comprising polymers formed therein, separating the treated vapor from said condensate, passing said treated vapor into indirect heat exchange relation with said treating material to reduce loss of heat from the treating material by radiation and subsequently condensing the treated vapor.

6. The method of refining cracked petroleum products which comprises passing the same in vapor form through a body of solid treating material capable of polymerizing the unstable, unsaturated compounds present in the vapor, draining from said body of treating material condensate comprising polymers formed therein, separately withdrawing the treated vapor from the body of treating material and passing the same into indirect heat exchange relation with said body of treating material to reduce loss of heat from the treating material by radiation, collecting condensate resulting from the heat exchange operation, condensing the treated vapor and adding thereto the condensate resulting from the heat exchange operation.

7. The method of refining cracked petroleum products which comprises passing the same in vapor form and under super-atmospheric pressure through a body of solid treating material capable of polymerizing the unstable, unsaturated compounds present in the vapor, draining from said body of treating material condensate comprising polymers formed therein, separately withdrawing the treated vapor from the body of treating material and passing the same into indirect heat exchange relation with said body of treating material to reduce loss of heat from the treating material by radiation, collecting condensate resulting from the heat exchange operation, condensing the treated vapor and adding thereto the condensate resulting from the heat exchange operation.

8. The method of refining cracked petroleum products which comprises passing the same in vapor form and under super-atmospheric pressure through a body of solid treating material capable of polymerizing the unstable unsaturated compounds contained in the vapor, draining from the body of treating material condensate including polymers formed therein, separately withdrawing the treated vapor from the body of treating material and passing the same into indirect heat exchange relation therewith to reduce loss of heat from the treating material by radiation, collecting the condensate resulting from the heat exchange operation, condensing the treated vapor and adding thereto said last mentioned condensate.

9. The method of obtaining motor fuel from petroleum which comprises subjecting the petroleum to cracking conditions, passing the cracked products in vapor phase through a body of solid treating material capable of polymerizing the unstable, unsaturated hydrocarbons present therein, draining from said treating material condensate comprising polymers formed in said material, withdrawing the treated vapor from the treating material and passing the same into indirect heat exchange relation with the treating material to reduce loss of heat from the treating material by radiation and subsequently condensing the treated vapor.

10. The method of refining cracked petroleum products which comprises passing the same in vapor phase through a body of solid treating material capable of polymerizing the unstable, unsaturated hydrocarbons present in the vapor, draining from said body of treating material condensate comprising polymers formed therein, separating the treated vapor from said condensate, passing said treated vapor around said body of treating material in heat exchange relation therewith to reduce loss of heat from said treating material by radiation and subsequently condensing the treated vapor.

11. The method of refining petroleum products containing unstable, unsaturated compounds which consists in passing such products in vapor phase through a body of solid treating material capable of polymerizing said unstable, unsaturated compounds, withdrawing from the body of treating material condensate comprising polymers formed therein, withdrawing treated vapor from said treating material and passing the same around the treating material in indirect heat exchange relation therewith to reduce loss of heat from said treating material by radiation, condensing the treated vapor and adding thereto the condensate resulting from the heat exchange operation.

12. The method of refining petroleum products containing unstable unsaturated compounds which consists in passing the same in vapor phase and under superatmospheric pressure through a body of solid treating material capable of polymerizing said unstable, unsaturated compounds, draining from said body of treating material condensate including polymers formed therein, withdrawing the treated vapor from said body of treating material and passing the same around the treating material in indirect heat exchange relation therewith to reduce loss of heat from said treating material by radiation and subsequently condensing the vapors.

13. The method of refining petroleum products containing unstable, unsaturated compounds which consists in passing the same in vapor phase and under super-atmospheric pressure through a body of solid treating material capable of polymerizing said unstable, unsaturated compounds, draining

from said body of treating material condensate including polymers formed therein, withdrawing the treated vapor from said body of treating material and passing the same around the treating material in indirect heat exchange relation therewith to reduce loss of heat from said treating material by radiation, condensing the treated vapor and adding thereto the condensate resulting from the heat exchange operation.

In testimony whereof, I have signed my name to this specification.

THOMAS T. GRAY.