(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 October 2012 (04.10.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/135474 A2

(51) International Patent Classification:
C10L 9/10 (2006.01) *F23K 1/00* (2006.01)
C10L 5/00 (2006.01)

(21) International Application Number:
PCT/US2012/031175

(22) International Filing Date:
29 March 2012 (29.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/078,631 1 April 2011 (01.04.2011) US

(71) Applicant *(for all designated States except US)*: **BAKER HUGHES INCORPORATED** [US/US]; P.o. Box 4740, Houston, TX 77210 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **VERDREE, Vera, T.** [US/US]; 3131 Memorial Court, Apt.14103, Houston, TX 77007 (US). **WALTHER, Leonard, E.** [US/US]; 1418 Morton Road, Russellville, TX 42276 (US). **KREMER, Lawrence, N.** [US/US]; 6 Greenridge Forest Drive, The Woodlands, TX 77381 (US). **BROWN, James, Michael** [US/US]; 6400 Camille Court, Lago Vista, TX 78645 (US).

(74) Agent: **LITTLEFIELD, Stephen, A.**; Baker Hughes Incorporated, P.O. Box 4740, Houston, TX 77210-4740 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) **Title**: METHOD FOR IMPROVING THE EFFICIENCY OF HEAT TRANSFER IN A FURNACE

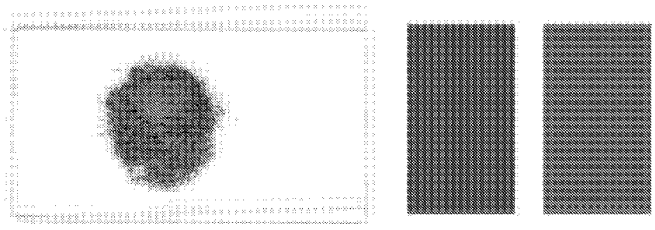


FIG. 1

(57) **Abstract**: An additive having as components, at least two metal oxides selected from iron, manganese, cobalt, and copper oxide, may be added to a fuel to reduce the brightness of ash produced therewith. Further, the additive serves to increase the heat transfer efficiency of furnaces.

WO 2012/135474 A2

TITLE: METHOD FOR IMPROVING THE EFFICIENCY OF HEAT TRANSFER IN A FURNACE

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to furnace systems. The present invention particularly relates to furnaces including systems for adding additives to fuels used therewith.

2. Background of the Art

[0002] Petrochemical plants, oil refineries, power generation stations, and the like; all utilize furnaces for heat generation. For centuries, man has relied upon the combustion of combustible materials, such as coal and wood, to provide heat energy. One of the most common methods for harnessing this heat energy is to use the heat energy to generate steam or heat other types of fluids.

[0003] Over the years, different types of furnaces or boilers have been developed for the combustion of coal, wood, and other combustible materials. In the late 1940's and early 1950's, there was a large decline in the demand for commercial and industrial solid fuel-fired systems due to the wide-spread availability of relatively cheap oil and natural gas sources. Thus, the oil and gas-fired systems substantially replaced the coal-fired systems until the gas and oil petroleum-based fuels became less plentiful during the 1970's. The petroleum shortage experienced during the 1970's and the very high prices of the late 2000's have made coal-fired and other solid fuel-fired systems very attractive once again.

[0004] In recent years, considerable emphasis has been given to solid fuel research, particularly in the area of burning solid fuels such as coal and wood without excessive pollutant emissions and with increased heat transfer efficiency. As the costs of oil and gas continue to escalate, the utilization of solid fuel systems (such as coal-fired systems) will continue to increase.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention is a process for treating fuels to increase heat transfer efficiency in furnaces comprising: contacting the fuel or ash from fuel combustion with an additive wherein the additive functions to increase radiant heat adsorption and the additive does not include a fluxing agent.

[0006] In another aspect, the invention is a process for treating a fuel to increase heat transfer efficiency in furnaces including contacting the fuel or ash from fuel combustion with an additive wherein the additive is a pigment comprising at least two (2) oxides selected from Fe, Cu, Co, and Mn oxides.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0007] The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee. The advantages and further aspects of the disclosure will be readily appreciated by those of ordinary skill in the art as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying figures:

Fig. 1 is a photograph of ash treated with 0.01% additive;

Fig. 2 is a photograph of ash treated with 0.02% additive;

Fig. 3 is a photograph of ash treated with 0.05% additive; and

Fig. 4 is a photograph of an untreated sample of ash.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] In one embodiment, the invention is a process for treating fuel or ash to increase heat transfer efficiency in furnaces. While coal is presently the most common fuel that may be used with the processes of the application, other fuels may also be used in other embodiments. For example, the process of the application may be used with coke, resid, heavy fuel oil, bitumen, and the like. Any fuel that burns to

produce an ash or residue that may improve heat transfer by being darkened may be used with process of the application.

[0009] The method of the application is employed in furnaces. One type of such a furnace, the stoker-fired furnace, was developed to burn relatively large particles of coal, up to about 1.5 inches in diameter. Later, another type of furnace, the pulverized coal-fired furnace, was developed for burning much smaller coal particles, e.g., where about 70% of the coal particles pass through a 200 mesh screen. Pulverized coal-fired furnaces have large steam generating capacities and are thus typically used in steam generating installations where at least 500,000 pounds of steam per hour are required. For example, the electric power generating industry has been one of the largest users of pulverized coal-fired furnaces, since large amounts of steam are required for the production of electric energy.

[0010] With either type of furnace, the coal added to the furnace combusts to produce heat. In some furnaces, the coal that does not instantly combust falls upon a grate on which the burning fuel bed resides. The grate moves, in some embodiments, at a very slow rate, e.g., from about 5 to 40 feet per hour, and eventually dumps the combustion by-products (namely, residual ash) into an ash pit or some other receptacle. Alternatively, the grate may be stationary but have the capability of being dumped at periodic intervals to remove the bed of accumulated ash. In some furnaces, the burning fuel bed is sluiced out.

[0011] One reason for the popularity of the spreader-stoker-fired furnace is its high superficial grate heat release rates of up to 750,000 BTU/hr-ft^2 and its low inertia due to nearly instantaneous fuel ignition upon increased firing rate. This high superficial grate heat release is obtained because of the relatively uniform distribution of the coal particles in the burning fuel bed on the grate, the relatively small depth of the layer of coal particles on the grate, and the intense combustion during the suspension phase above the burning fuel bed. The low inertia allows the spreader-stoker-fired furnace to respond rapidly to load fluctuations in steam demand, and hence in boiler load, which are common in industrial applications.

[0012] In the practice of one embodiment of a method of the application, the coal to be burned may be treated with an additive. In one embodiment, the additive is a

pigment including oxides of iron, copper, cobalt and manganese. This pigment interacts with coal ash to darken the ash.

[0013] By darkening the coal ash, heat transfer is improved within the furnace. While not wishing to be bound by any theory, it is believed that radiant heat is more efficiently absorbed by the ash clinging to the walls of the furnace when the ash is dark. Especially when that surface is a heat exchanger tube, the radiant energy may be transferred to the heat transfer medium along with the normal convected heat resulting in more heat reaching the heat transfer medium and thereby improving the efficiency of the furnace.

[0014] The additive of the disclosure does not include a fluxing agent. For example, there is no need to add a fluxing agent such as a borate. Fluxing agents in general and borate fluxing agents in specific are known to those of ordinary skill in the art. One advantage of the additive of the disclosure is that it stays with the ash without the need for a fluxing agent. Other pigments, if not affixed to coal ash, may be problematic. For example, some pigments may travel up the stack of a coal furnace and cause opacity problems. Other pigments may present disposal problems.

[0015] While the additive of the disclosure may be used with any type of coal, it is desirably utilized with coal that has high levels of calcium. Such coal produces a very light colored ash and even a very small amount of additive may provide for a significant improvement in heat transfer efficiency.

[0016] The additive of the invention is an inorganic pigment that includes at least two (2) of the oxides of copper, iron, cobalt, and manganese. In some embodiments all 4 metals may be present. The additive may, in some embodiments, have from about 15 to about 60% by weight (as metal) copper oxide; from about 20 to about 70 % by weight (as metal) manganese oxide; from about 20 to about 70 % by weight cobalt; and from about 5 to about 30% by weight (as metal) iron oxide. In other embodiments, the additive may have from about 25 to about 45% by weight (as metal) copper oxide; from about 35 to about 60 % by weight (as metal) manganese oxide; from about 35 to about 60 % by weight (as metal) cobalt; and from about 10 to about 25% by weight (as metal) iron oxide. In another embodiment, the additive will have at least three (3) of the above referenced oxides.

[0017] The additives of the disclosure may be in any form that would be known to be useful to one of ordinary skill in the art of producing heat using a furnace. For example in one embodiment, the additive can be a blend of three or more powdered metal oxides. In another example, the metal oxides may be in the form of a pellet formed by heating mixtures of the metal oxides. In some embodiments, the additive may be applied to coal or introduced into a furnace as a powder and, upon being subjected to the heat of a furnace, become a ceramic-like material.

[0018] In one embodiment, at least one of the metal oxides used to form the additive of the application is sintering the metal oxide at a temperature just below its melting temperature. For example, CuO may be heated at near its 1235°C melting point to form pellets. In another embodiment, CuO and one or more of the other metal oxides may be heated at a temperature near the lowest of the melting points of the metal oxides present to form a pellet. In still other embodiments, the metal oxides may be heated up to nearly their decomposition points. In any of these embodiments, very small pellets so formed may be used with powered oxides to form the additive.

[0019] Whether formed as a pressed pellet, sintered pellet, a mixture of pellets and powder or any combination thereof, the form of the additive may be small enough to readily form a comparatively dark surface on the heat absorbing surfaces of the furnace. The size of the individual pellets or grains of the additive may vary with the conditions to which they are exposed during the combustion process.

[0020] The additive may be added to coal or it may be added directly to a furnace as coal is being fed as fuel. In one embodiment, the additive is sprayed onto coal as a liquid prior to it being pulverized. In one such embodiment, a nozzle is used to perform the spraying. In another embodiment, the additive is sprayed onto coal as a liquid after it has been pulverized. In still another embodiment, the additive is introduced into coal as a solid. Another embodiment of the method of the disclosure includes introducing the additive as a solid prior to the coal being pulverized. The additive may be introduced into coal or a furnace using any method known to be useful to those of ordinary skill in the art.

[0021] The additives may be applied to the fuel, as discussed in regard to coal, and/or applied directly to ash after combustion is partially or fully complete. Generally, this may be performed by selecting where in the furnace the additive will

be introduced. In most furnace types, the further downstream from the burning fuel that the additive is introduced, the more likely that the additive will come into contact with fuel ash rather combusting fuel.

[0022] The methods of the disclosure may be used advantageously to improve power plant operations. In some applications, more power may be produced per unit of coal. In other applications, the need for removing soot from the inside of a furnace may be reduced. In still other applications, both of these advantages may be noted.

EXAMPLES

[0023] The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

Example 1

[0024] An inorganic pigment including iron, manganese, and copper oxides; available from the FERRO Corporation under the trade designation F-6331-2 is used to darken coal ash. A high calcium lignite coal is admixed with the additive at a concentration of 0.01%. The ash is burned and then scanned. The resulting scan is evaluated using an HSB (Hue, Saturation, and Brightness) model. The HSB model represents points in an RGB color model that attempt to describe perceptual color relationships more accurately than RGB, while remaining computationally simple. HSB allows colors to be interpreted as tints, tones and shades. By converting the samples into this electronic color model it is possible to measure the difference in actual brightness, while keeping hue and saturation independent. The scan may be seen below in Fig. 1. The sample is measured and has a brightness of 44%

Example 2

[0025] Example 1 is repeated substantially identically except that 0.02% of additive is used. The scan may be seen below at Fig. 2. The brightness is measured as 37%.

Example 3

[0026] Example 1 is repeated substantially identically except that 0.05% of additive is used. The scan may be seen below at Fig. 3. The brightness is measured as 27%.

Comparative Example (Control)

[0027] Example 1 is repeated substantially identically except that no additive is used. The scan may be seen below at Fig. 4. The brightness is measured as 68%.

TABLE

Sample ID	[Additive in wt. %]	Brightness %	% Change
Ex 1	0.01	44	35.3
Ex 2	0.02	37	45.6
Ex 3	0.05	27	60.3
Control	--	68	--

Hypothetical Example

[0028] A power plant driven by a coal fired furnace is operated using untreated coal. Variables recorded during the operations include the rate at which coal is introduced into the furnace, megawatts of power produced, and the frequency of "soot-blows." This latter term refers to the process where soot deposited on the furnace tubes is blown from the furnace using a blower. After the power plant is operating at a steady load, the additive of Example 1 is introduced on to the coal being fed into the furnace by spraying a solution/dispersion of the additive onto the coal. After the introduction of the additive into the furnace, and allowing the power plant to return to operation at a steady load, it is noted that more megawatts of power is produced per unit of coal, and fewer soot-blows are required per shift.

CLAIMS

What is claimed is:

1. A process for treating a fuel to increase heat transfer efficiency in comprising contacting the fuel or an ash resulting from fuel combustion with an additive wherein the additive functions to increase radiant heat adsorption as compared with an otherwise identical process absent the additive; and
the additive does not include a fluxing agent.

2. The process of Claim 1 wherein the additive is a pigment comprising at least 2 oxides selected from Fe, Cu, Co, and Mn oxides.

3. The process of Claim 2 wherein the pigment comprises Fe, Cu and Mn oxides.

4. The process of Claim 3 wherein the pigment comprises from about 15 to about 60% by weight (as metal) copper oxide; from about 20 to about 70 % by weight (as metal) manganese oxide; and from about 5 to about 30% by weight (as metal) iron oxide.

5. The process of Claim 4 wherein the pigment comprises from about 25 to about 45% by weight (as metal) copper oxide; from about 35 to about 60 % by weight (as metal) manganese oxide; and from about 10 to about 25% by weight (as metal) iron oxide.

6. The process of Claim 2 wherein the pigment comprises Fe, Cu and Co oxides.

7. The process of Claim 6 wherein the pigment comprises from about 15 to about 60% by weight (as metal) copper oxide; from about 20 to about 70 % by weight (as metal) cobalt oxide; and from about 5 to about 30% by weight (as metal) iron oxide.

8. The process of Claim 7 wherein the pigment comprises from about 25 to about 45% by weight (as metal) copper oxide; from about 35 to about 60 % by weight (as metal) cobalt oxide; and from about 10 to about 25% by weight (as metal) iron oxide.

9. The process of Claim 1 wherein the additive is a pigment comprising Fe, Cu, Co, and Mn oxides.

10. The process of Claim 1 wherein at least one of the metal oxides is in the form of a pellet prepared by sintering prior to being applied to the fuel or introduced into the furnace.

11. The process of Claim 10 wherein two or more of the metal oxides are admixed and then sintered prior to being applied to the fuel or introduced into the furnace.

12. The process of Claim 1 wherein the additive is introduced to the fuel prior to combustion.

13. The process of Claim 12 wherein the additive is sprayed onto the fuel.

14. The process of Claim 13 wherein the fuel is coal and the process further comprises pulverizing the coal, and the additive is sprayed onto the coal prior to pulverizing.

15. The process of Claim 13 wherein the fuel is coal and the process further comprises pulverizing the coal, and the additive is sprayed onto the coal after or concurrently with pulverization.

16. The process of Claim 12 wherein the additive is admixed with the fuel as a solid.

17. The process of Claim 16 wherein the additive is admixed with the fuel prior to or concurrently with pulverization.

18. The process of Claim 1 wherein the additive is introduced to the fuel concurrently with combustion.

19. The process of Claim 19 wherein the additive is sprayed into the furnace.

20. A process for treating a fuel to increase heat transfer efficiency in furnaces comprising: contacting the fuel with an additive wherein:
the additive functions to increase radiant heat adsorption of ash;
the additive does not include a fluxing agent; and
the additive is a pigment comprising at least 2 oxides selected from Fe, Cu, Co, and Mn oxides.

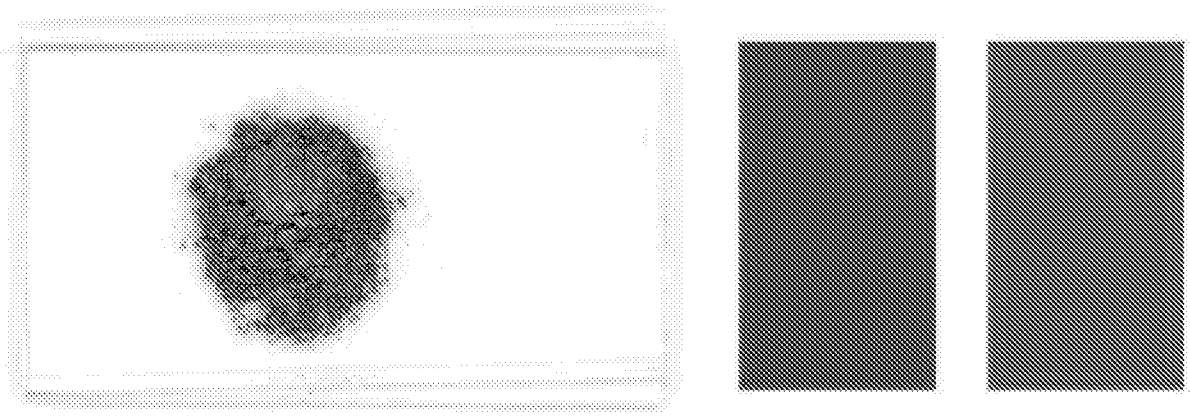


FIG. 1

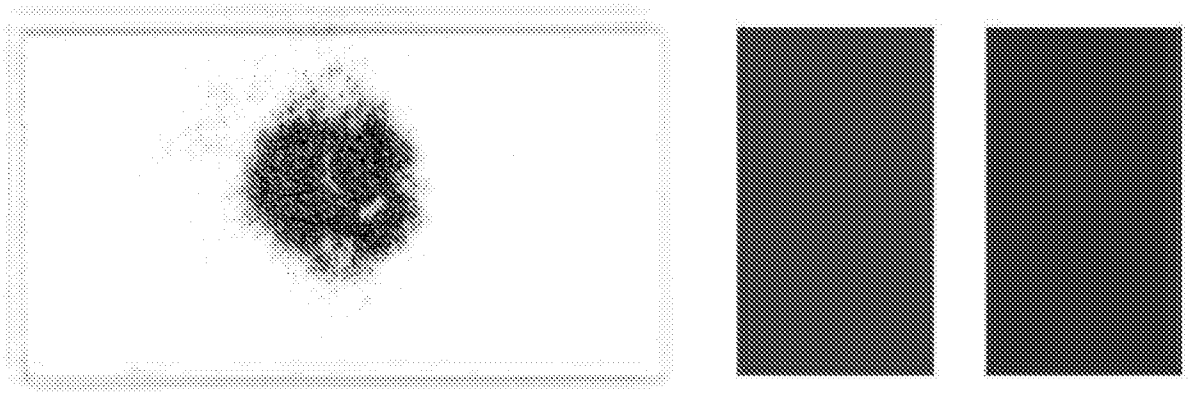


FIG. 2

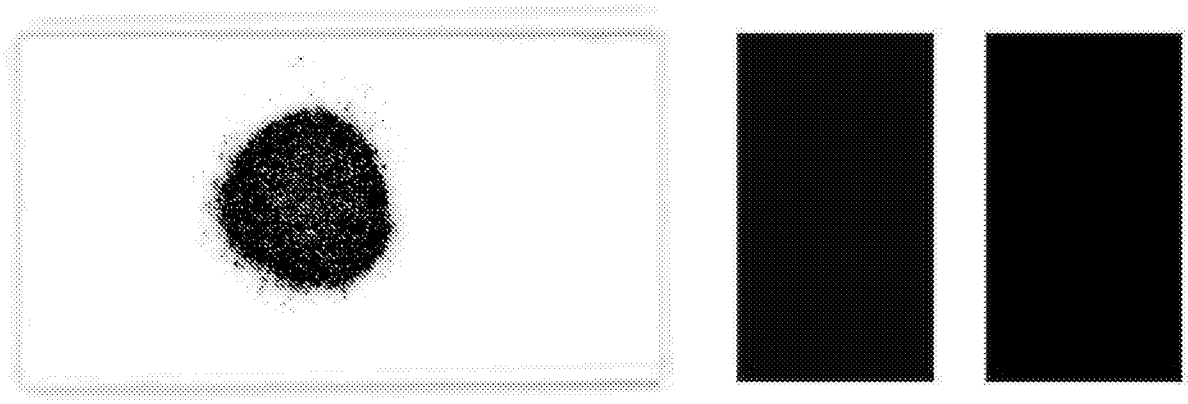


FIG. 3

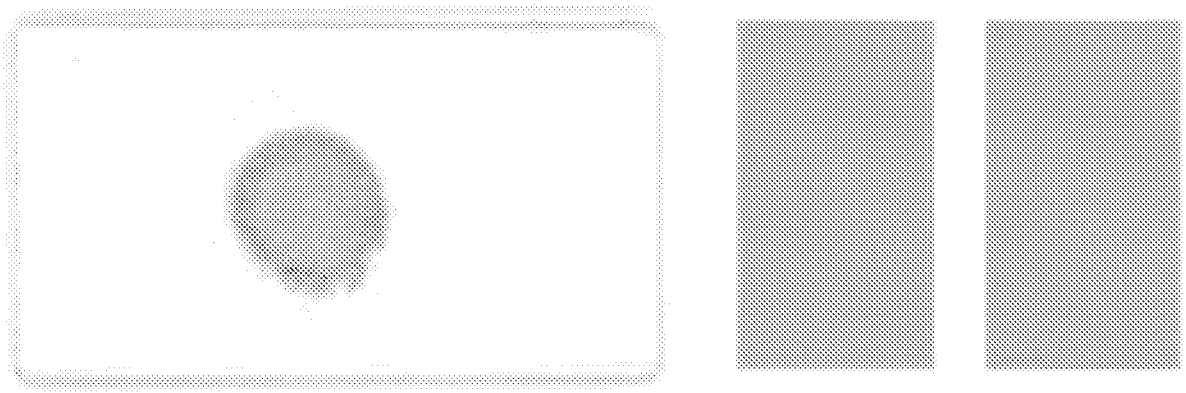


FIG. 4