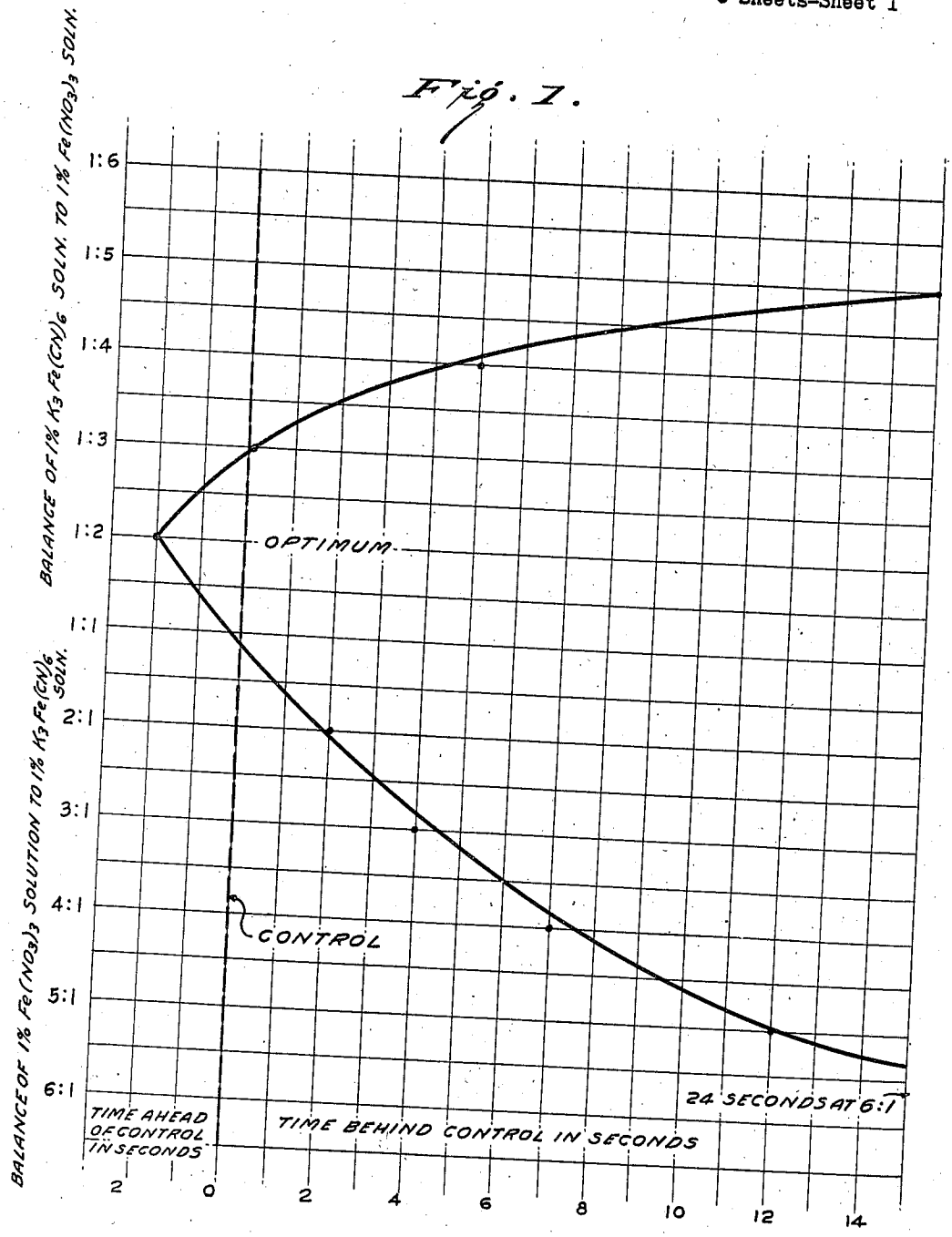
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METHOD OF BLUING COAL

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Fig. 1.



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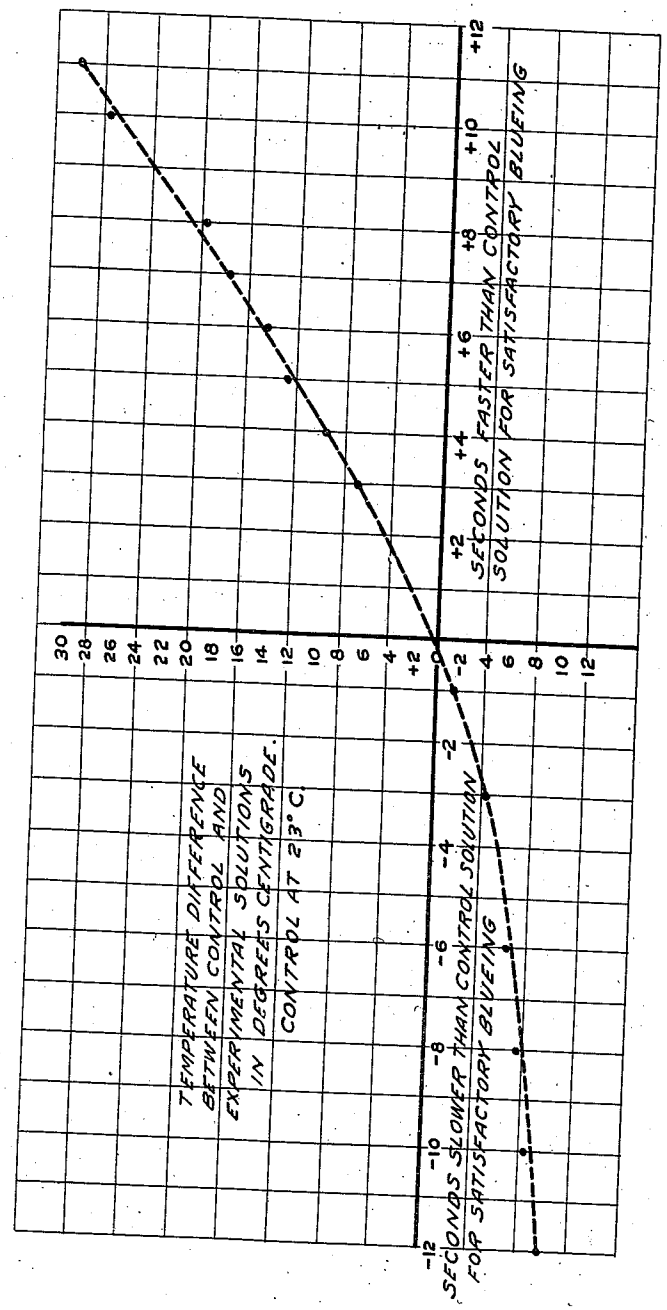


Fig. 2.

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METHOD OF BLUING COAL

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Fig. 5.

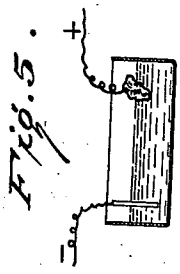


Fig. 4.

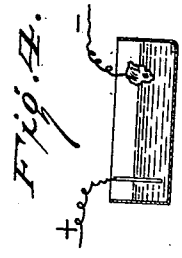


Fig. 3.

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METHOD OF BLUING COAL

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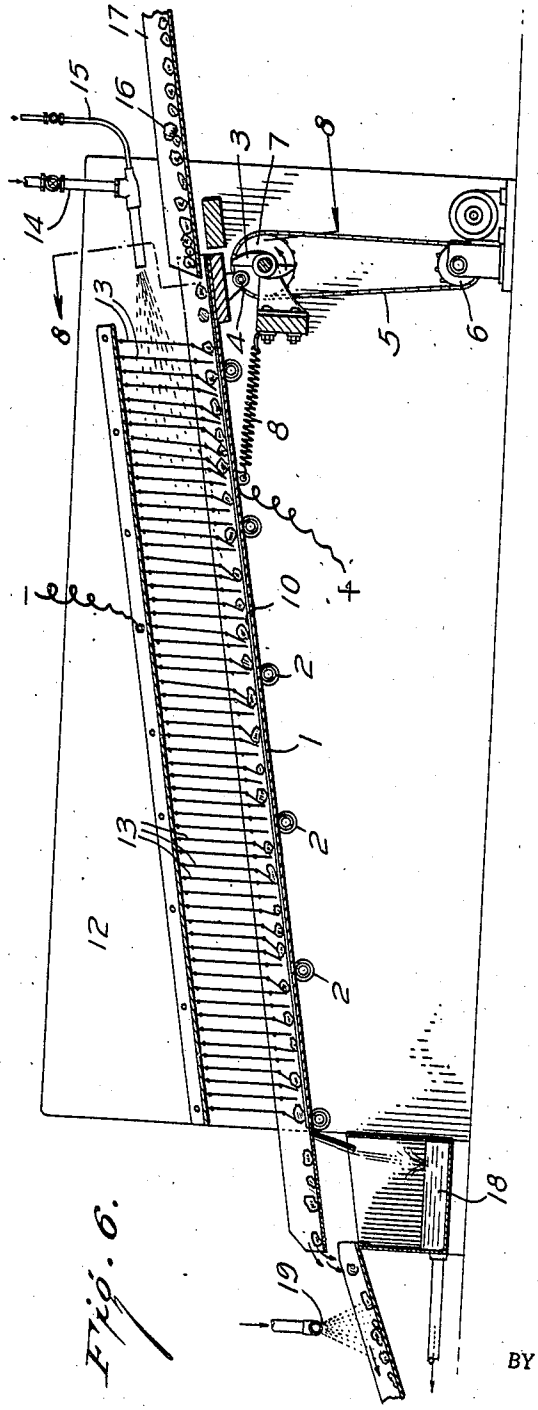


Fig. 6.

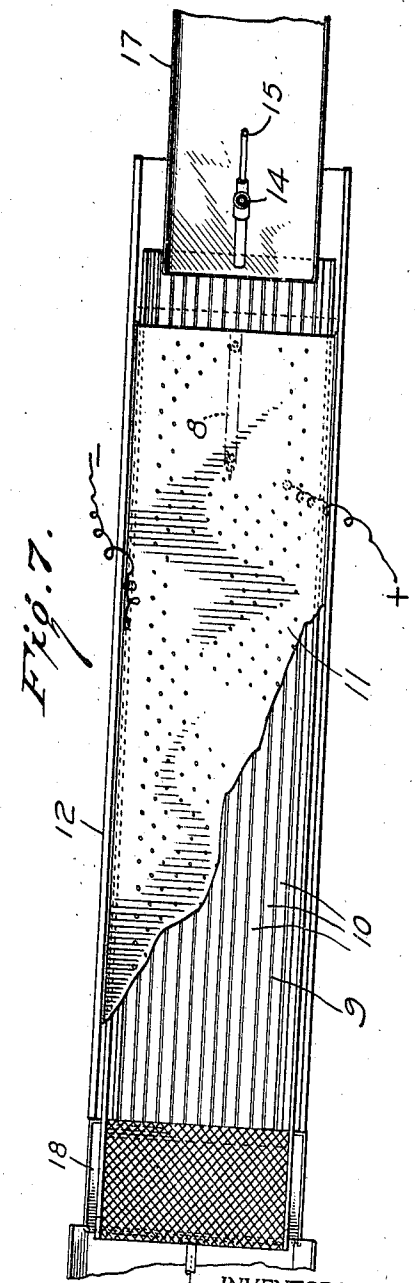


Fig. 7.

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Fig. 8.

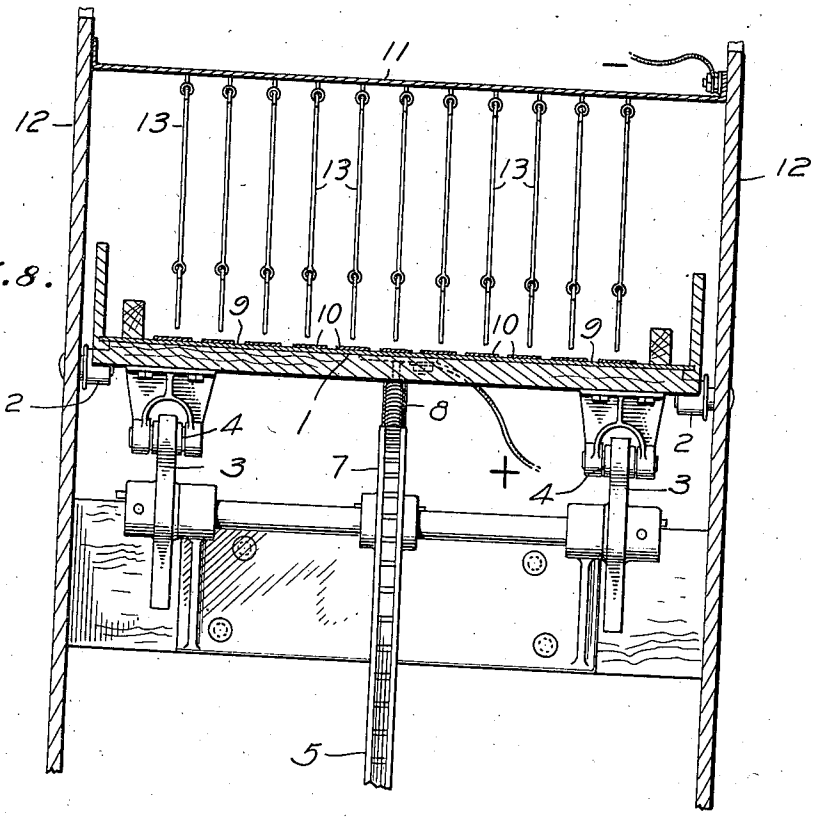
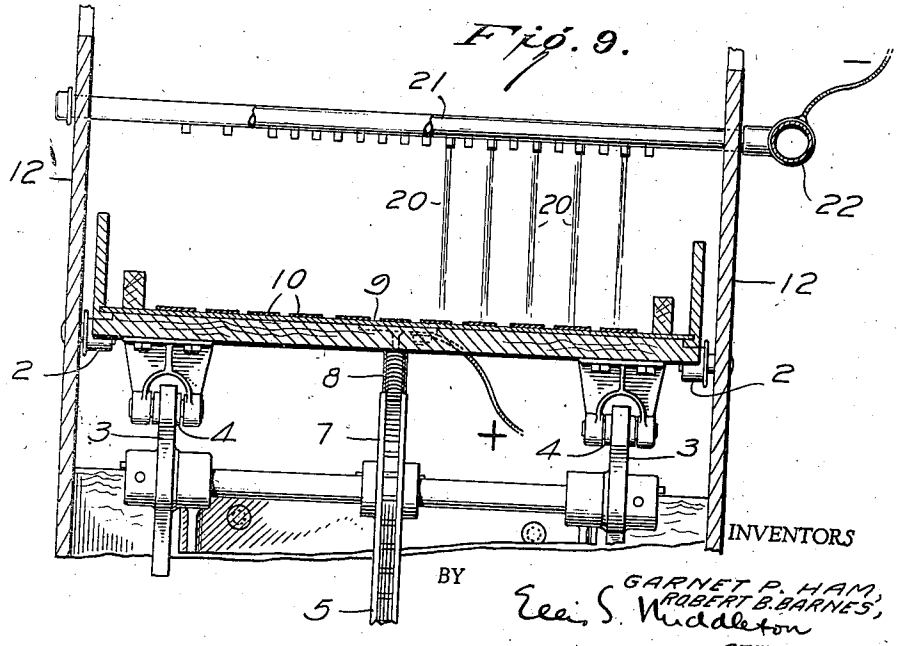


Fig. 9.



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Patented Mar. 2, 1943 2,312,898

UNITED STATES PATENT OFFICE

2,312,898

METHOD OF BLUING COAL

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Application January 9, 1941, Serial No. 373,712

4 Claims. (Cl. 204—131)

The present invention relates to a method of electrolytically depositing iron blues upon coal surfaces.

The principal object of the present invention is to carry out the above method under such conditions as to give a deposit of substantially uniform color, in a minimum space of time, using optimum ratios and concentrations of reactants, all with due regard to chemical color stability and resistance to abrasion.

There are a number of disclosures in the art of the application of iron blues to coal, such art using alkali or alkaline earth metal ferricyanides and soluble ferric salts where coal was subjected to a spray of, or immersed in, the combined solutions. These methods, while ordinarily satisfactory, are not always competitive from the standpoint of cost as there are a number of cheaper ways available to apply a distinctive blue color to a coal surface.

A study of the mechanism of the coloring reaction involved in iron blues has led to a number of very interesting discoveries, some of which are contradictory to published data.

It was, therefore, one of the objects of the invention to exhaustively study this subject in order to determine optimum conditions under which a satisfactory iron blue color could be obtained on a coal surface at minimum cost.

It has been discovered that among the important considerations in accomplishing the above object, are such items as particular ferric compounds, reactant ratio and dilution, reaction temperature, the pH of the reacting solution and the carrying out of the reactions under the influence of D. C. electrical potential, while the coal is, or is in contact with, the negative electrode. This last feature is by far the most important in that when the reaction is carried out electrolytically under controlled conditions, the speed of formation of the iron blue on the coal surface is materially increased. This being true, other factors may be adjusted to suit commercial conditions, taking advantage of the speed control afforded by the electrical impulse.

The invention, therefore, contemplates in one of its broad aspects the electrolytic deposition of iron blues on coal from solutions of alkali metal ferricyanides and ferric nitrate, chloride or sulfate, while maintaining the coal to be colored constantly within unidirectional electrical circuit. While conditions of choice of reactants, their dilution, the temperature of the reaction and the pH are all important, yet these are secondary as compared with the use of an electrical circuit.

The invention further contemplates the novel steps of the methods and conditions under which the steps are carried out, all as more fully hereinafter described and diagrammatically shown in the accompanying drawings.

In the drawings:

Fig. 1 is a graph showing the result of bluing time as compared with a control plotted against a ratio of ferricyanide and ferric nitrate;

Fig. 2 is a graph showing the effect of temperature on bluing time;

Fig. 3 is a graph showing the result of subjecting coal to an electrical potential while subjected to the bluing reagent;

Fig. 4 is a diagrammatic representation of a piece of coal used as a negative electrode in the bluing bath;

Fig. 5 is a diagrammatic representation of a piece of coal used as a positive electrode in the bluing bath;

Fig. 6 is a sectional elevation of an apparatus adapted to carry out the present invention;

Fig. 7 is a plan view of the device of Fig. 6;

Fig. 8 is a sectional view along the line 8—8 of Fig. 7;

Fig. 9 is a sectional end view of a modified form of device.

At the outset, it has been discovered after a considerable and extended experimentation that anthracite coal varies in its electrical conductivity to a tremendous extent. For example, samples of coal from different collieries have been found to have electrical resistance (D. C.) through samples about two inches thick over a range from 100 ohms to as high as 13 million ohms. The present invention is particularly applicable to anthracite coal having an electrical resistance (D. C.) of from 100 to 800,000 ohms, for it is within this range that the apparent effect of the electrolytic method is most noticeable.

The color of a film of iron blue on coal is a function of the applied layer thickness. This has been definitely determined by spectrophotometric analysis. The amount produced is also a function of time and solution temperature. As processing times increase, the color of the applied film goes through the shades of gold, bronze, purple, violet, blue, blue-green, green and green-yellow. Beyond this point, second order interference results.

In determining the effect of various conditions upon the bluing of coal by the herein described methods, matched samples of freshly fractured

coal pieces were obtained by cracking a lump of coal and using the two matched faces, one for the control and the other for the experiment. This method of experimenting was determined to the best by reason of the fact that initial work determined that unless the surface to be treated was a freshly fractured one, the results were non-uniform and undependable. After treatment of both surfaces for the prescribed time period, the pieces were quickly water washed to stop the reaction and then dried in a current of air.

A 1% solution of reactants was arrived at as representing optimum conditions, both from the standpoint that considerable volume was required to treat large masses of coal and also from the standpoint that commercial practice has adopted this concentration as a standard.

Experiments have demonstrated that of the soluble ferric salts, the nitrate, chloride and sulfate give the best results with alkali metal ferricyanides in the order named. Of these three, the ferric nitrate was outstanding in that it required less time to produce a desired color than with either the chloride or the sulfate. This having been determined, further experiments were made only with the nitrate. As to the alkali metal ferricyanide, the sodium salt is preferred because of cheapness.

In an effort to determine the effect on bluing when varying proportions of the component solutions, it has been found that by increasing the ratio of 1% ferric nitrate solution to 1% ferricyanide solution through a range of from 1:1 to 1:6, the bluing time decreased at a 1:2 ratio but then became gradually decadent at higher ratios because of a reduction in pH value.

For instance, a certain coal blued in the 1:1 control bath in 15 seconds, while a similar type coal treated in a 1:2 ratio solution of ferricyanide to ferric nitrate blued in 13 seconds. Further changes such as a ratio of 1:5 required 15 seconds longer to blue than the control or 30 seconds in all. From the graph of Fig. 1, the effect of this dilution is clearly shown where a ratio of 1:2 may be considered as optimum.

As showing the effect of temperature variations, certain coals blued with a control using 1:2 ratio solution at 23° C. in 15 seconds. When using a matched surface, and increasing the temperature of the bath, the bluing time to obtain the same color decreased. For instance, where the temperature of the bluing solution was 10° higher than the control, or 33° C., the time required to match the control color was four seconds faster or only eleven seconds. Again, when the temperature of the bluing solution was 51° C., only four seconds was required to match the color of the control specimen.

On the contrary, when the temperature of the solution was 13° C., it required 12 seconds longer to reach the color acquired by the control, or 27 seconds.

The pH value of the mixed solution is a factor toward the speed of bluing coal as it controls the formation of the ferri ferricyanide ions which are essential in the process.

As illustrating this, it has been determined that the pH value of a bluing solution, that is, one part by volume of 1% alkali metal ferricyanide and 1 part by volume of 1% ferric nitrate solution is 2.3 at 25° C. Lowering this value by the addition of a mineral acid causes a decided slowing of the bluing reaction. For instance, when the pH was made 1.3 by nitric acid, the bluing time of a bath which had previously been 15 seconds was increased to over 30 seconds. This effect was not confined to nitric acid alone but appeared to be typical not only for all mineral acids but also is the indirect effect of a misadjustment of the reactants themselves insofar as the presence of an excess quantity of ferric nitrate is concerned as this substance is acidic in character, as clearly shown in Fig. 1.

As a consequence of the above, the bluing time may be slowed down where desired by the addition of acid or an excess of ferric nitrate but if a minimum bluing time is to be observed, the pH should not be adjusted beyond that normally obtaining with the desired proportion of ferricyanide to ferric nitrate.

The above study was thought necessary in order to determine the most favorable conditions leading up to the bluing of coal in the shortest space of time so that these conditions could be used as a standard to determine the effect of an electric field upon the reaction.

Fig. 3 shows the effect as to bluing time while carrying out the reaction within a D. C. electrical circuit as compared with a non-electrical control. In these experiments, a bath of freshly mixed 1% sodium ferricyanide and 1% ferric nitrate, in the proportion of 1:2 at a temperature of 23° C. was used. The coal piece to be tested was made the negative electrode while a positive electrode was formed of a sheet of aluminum immersed in the solution as shown in Fig. 4.

From Fig. 3, it will be noted that when the reaction was carried out under a potential of as little as three volts, a considerable decrease in the bluing time was obtained over a non-electrical control to obtain the same degree of color. The current potentials mentioned on the figure are D. C.

From this figure, it will be noted that as the potential increased generally speaking, the bluing time decreased. While there is some variation in the uniformity of this decrease as potential increases, this is undoubtedly due to the fact that the particular pieces of coal tested varied in their electrical resistance.

When the polarity of the coal piece and the aluminum electrode was reversed as in Fig. 5, no bluing was obtained, even after an extended period.

As a result of the discovery that color could not be obtained at all unless the coal piece was the negative electrode, it was not surprising to find that when alternating current was substituted for direct current, no bluing was obtained.

From the above, it has been definitely determined that, all things being equal, if the coal piece is blued while being subjected to the influence of a D. C. electrical circuit where the coal is, or is in contact with, the negative electrode, the bluing time may be decreased in reaching a required standard of color as compared to a completely non-electrical method.

In adapting the above experimental procedures to commercial operations, the apparatus shown in Figs. 6 to 9 were used. This apparatus consists generally of an inclined shaker chute actuated by a cam driven from a speed controlled motor, the rebound being caused by a spring. Reagent nozzles are provided at various points above the surface of the coal chute and connected to a suitable source of mixed reagent.

One form of device is shown in Fig. 6 as consisting of a trough 1 supported upon a series of rollers 2, a shaking action being secured through rotary cam fingers 3 against cam rollers 4. A

chain 5 connects a motor-driven sprocket 6 with the sprocket 7 which actuates the cam fingers. Rebound is accomplished by means of the spring 8.

The bottom of the trough 1 is faced with a metal sheet 9 and overlaid with dielectric strips 10 such as a molded plastic or the like. A bus bar 11 extends between the stationary sides 12 of the apparatus, the former having depending therefrom a series of electrodes 13. The bus bar 11 is made the negative terminal of a direct current circuit while the metal plate 9 is made the positive terminal.

The reagent is supplied through pipe 14 while air under compression enters through jet 15 so as to develop a good spray projected in the direction of travel of the coal pieces.

Coal 16 is moved down a stationary chute 17 into a trough 1. Due to the fact that the trough is being constantly shaken, the coal pieces move stepwise down the former.

As shown in Fig. 6, each piece of coal completes the circuit between the depending negative electrode 13 and the metal plate 9, when the coal is wet with the reagent spray although the coal itself is out of contact with the plate 9. As there are a large number of these depending electrodes, each piece of coal in its travel down the chute is continuously bathed in reagent and in an electrical field. Excess reagent flows from the bottom of the trough 1 into the tank 18 where it is either disposed of or recovered for reuse. The coal drops off the end of trough 1 and passes under water spray 19 so as to completely remove excess reagent. The coal is then air dried.

A modified form of apparatus is shown in Fig. 9, which differs from that of Figs. 6, 7 and 8 only in that the overhead electrode takes the form of a series of continuous reagent streams 20 emerging from pipe 21 connected to the supply manifold 22. The manifold is connected to a source of direct current as the negative electrode. In this way, the pieces of coal as they progress down the chute are constantly bathed in liquid and due to the fact that the streams 20 are unbroken, are also constantly in the electrical circuit.

In one experiment, the apparatus of Fig. 9 was used in which, however, instead of the continuous unbroken streams of reagent 20, the reagent was sprayed as individual particles upon the coal, the spray nozzles being the negative electrode. After repeated failures to decrease the bluing time of coal in this apparatus over a similar non-electrical method, using voltages of from a fraction of a volt to 700 volts, it was definitely determined that the reason for this failure was that there was no flow of current between the spray nozzle and the surface on which the coal rested. Regardless of the fineness of the reagent spray or the distance between the point of emergence of the spray and the coal surface, it was impossible to establish a circuit by this method. It was only when the stream of reagent was continuous that the circuit was established and under these circumstances, no difficulty was encountered in decreasing the bluing time. The optimum current strength was found to be between one and 50 volts. Even a fraction of one ampere was found to be sufficient, it being only necessary to cause a current flow at the voltage used.

The above has clearly demonstrated the fact that to be blued electrically, the coal must not only be the negative electrode but it must be continuously in the electrical circuit. Under these circumstances, less time is required to reach a standard color with a ferricyanide-ferric salt mixture than where a non-electrical condition exists.

While the invention has been shown and described with specific reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims.

We claim:

1. A method of bluing coal which includes applying thereto a solution containing a ferricyanide and a ferric salt while continuously passing a direct current from a positive electrode, through the solution, to the coal, the latter serving as the negative electrode.

2. The method of claim 1 in which the ratio of ferricyanide to ferric salt is substantially 1:2.

3. The method of claim 1 in which the current potential is from one to fifty volts.

4. The method of claim 1 in which the ratio of ferricyanide to ferric salt is substantially 1:2 and the current potential is from one to fifty volts.

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