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METHOD AND COMPOSITION FOR TREATING COAL

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This application is a continuation in part of our application Serial No. 744,940 filed September 21, 1934.

Our invention relates to coal and particularly to a method and composition for treating coal whereby, among other things, it is rendered dustless and the particles thereof are prevented from freezing solidly together.

In addition, we have also discovered that our method and composition improve the appearance of the coal, reduce degradation and segregation during handling and storing, reduce the formation of fly-ash during combustion, and practically eliminate the damage done to mining machinery and railroad equipment by highly corrosive treating solutions heretofore known in the art.

Even before the introduction of clean competitive fuels, like oil and gas, coal loaded into railroad cars for shipment from the mines was usually in a more or less wet condition. The adhering moisture was not merely an incident to the washing operation, necessary to certain types of coal for the removal of foreign matter and naturally present acidic compounds, but was also intended to impart to the coal a shiny appearance and to render it dustless. Thus, even in drymining, the coal was frequently wetted at the loading booms to minimize the dust nuisance. Since the adhering moisture usually evaporated before the coal reached its final destination, wholesalers and retailers repeated the wetting, and even the consumer who appreciated the improved combustion resulting from limited amounts of water sprinkled his fuel before feeding it into the furnace.

While the above mentioned advantages were derived from wetting the coal, there was considerable inconvenience and some expense attendant upon the repeated sprinklings, and there was the danger that the particles of coal would freeze solidly together in cold weather. Coal so frozen is difficult and sometimes impossible to unload from cars and other containers and the cost of the delay, the labor involved in breaking up the blocks when solidly frozen, and the increased loss of fuel through rough mechanical handling and the disintegrating influence of water freezing within the pores of the coal, must be borne by both the seller and the buyer. Furthermore, coal so frozen becomes gray and dull, and is no more dustless than dry coal.

It has been proposed to prevent coal in railroad cars from freezing by sprinkling it with flakes of calcium chloride, but this method is practically worthless in zero weather. The antifreezing material is not properly distributed throughout the coal and, moreover, the calcium chloride imparts to the coal a gray-white appearance which has made customers hesitate to accept it as a good quality fuel. Intended only to reduce the amount of labor usually involved in unloading frozen coal shipments, this method is of little, if any, value in preventing dust.

As long as the public accepted dirty coal as a necessary evil, the producers gave little thought to making their product dustless. However, after oil and oil burners had invaded the market and the consumer became acquainted with the advantages of clean fuel, elimination of dust became of primary importance.

The hygroscopic, and even more so the deliquescent properties of certain inorganic compounds, of which calcium chloride is a typical representative, suggested the latter almost at once for dust treatment of coal. The results were not as satisfactory as expected. Although it stopped the dust nuisance for some time after application, the treatment was not lasting. True enough, under ideal weather conditions—moderate temperature, comparatively high humidity and absence of precipitation—the fuel usually reached the customer in a fairly clean state. However, during the warmer seasons the coal soon lost its original luster, becoming dull and gray and quite dusty, and rain proved to be entirely fatal to the dust treatment. In practice, this meant that the coal could never be stored in the open air for any length of time. More damaging even to the continued acceptance of calcium chloride solutions by the coal operators were the corrosive properties of this material. Every piece of iron or steel equipment within the vicinity of the sprays or the freshly treated coal—like pipes, loading booms, railroad cars and rails—corroded with alarming rapidity. Never entirely satisfactory as a dust preventing compound, the use of calcium chloride in liquid form was finally abandoned because of its corrosiveness.

It has since been proposed to render coal dustless by coating it with oils of the paraffin series. While with the introduction of this new method the excessive corrosion of mining and railroad equipment was definitely stopped, other disadvantages of equally serious nature became evident. Outstanding among these is the inflammability of atomized oils including those of higher viscosity. For the sake of economy and uniform distribution all coal to be treated by this method must pass through a fine mist of oil which is

produced by sprays of high dispersing power. The danger of this procedure is obvious. To put it bluntly, attached to the end of the loading booms are oil burners waiting to be ignited by an incidental spark or a carelessly thrown glowing object. Moreover, the fire hazard is not confined to the vicinity of the loading booms for wind and drafts carry the fine mist of oil over the whole tipple or breaker where it settles and soaks into every wooden structure it may encounter. Quite a number of tipple fires have been reported which can directly or indirectly be traced to oil.

In spite of all care, oil escaping in the form of mist and drops, during spraying and changing of railroad cars, respectively, contacts the safety equipment of the cars preventing it from properly functioning. To safeguard against property damage and injury to human life, an important railroad company sent out only recently a form letter to coal operators in the West Viginian coal fields wherein these dangers were discussed and warnings given that more drastic steps would be taken, if the cause for the complaint were not eliminated in the near future.

With varying temperatures, oils are subject to great changes in viscosity. Consequently, oils have to be heated prior to application in severe winter weather, and pump pressures have to be watched and adjusted with even minor changes in temperature.

In addition to the disadvantages of oil treatment just discussed, oil treated coal is slightly odorous and shows a tendency to leave an oily smudge on concrete or wooden storage bins. The oil tends to increase the smoke ordinarily emitted during combustion, and it does not prevent wet coal from freezing solidly together in railroad cars during cold weather. In all, it is a source of trouble to producer, shipper, seller and consumer alike.

The principal object of this invention is to provide an improved, non-inflammable, odorless and substantially non-corrosive composition of matter, and an improved method of treating coal efficiently and cheaply, whereby it will be made substantially permanently clean and dustless, more resistant to degradation, more lustrous, less inclined to the formation of fly-ash during combustion, and whereby the particles thereof will be prevented from freezing solidly together, even in severe winter weather. These desirable results are attained by combining such materials as inorganic salts which have the properties to lower substantially the freezing point of the water and to attract and retain moisture, with a substance or substances adapted to reduce substantially the inherent corrosiveness of such salts, assist their power of retaining moisture, prevent them from crystallizing on the coal in warm weather and, through their ability of forming semi-solid films, assist materially in the allaying of dust.

Broadly, the desirable objects of this invention are obtained by dissolving in water a major portion of a substance adapted to lower substantially the freezing point thereof and to attract and to retain water, and a minor portion of a colloid capable of forming a gel with water which will not only prevent the anti-freezing material from crystallizing but will substantially inhibit the corrosive properties of such salt solutions and produce a finished composition which will impart to the coal a glossy, smooth and lasting finish enhancing the natural black color of the product.

While there are many salts which may be employed to lower the freezing point of the water, such as zinc chloride, magnesium chloride, calcium chloride, ammonium chloride, and other crystallizable compounds, or a mixture of the same, we prefer, because of its efficiency and cheapness, to use calcium chloride. Likewise, while there are many suitable organic colloids like gelatine, starch, agar-agar, ammoniacal casein, and others capable of forming a substantially transparent jelly or film in the presence of water, we prefer to use a starch and particularly cornstarch. For reasons which will be explained later on we prefer especially to use starch containing up to 6% of naturally incrusted glutinous matter.

It will be noted that all of the aforesaid colloids are hygroscopic but non-deliquescent. If colloids are employed which are deliquescent, the strong film which prevents the weak particles of coal from crumbling would not be produced, and applicants' invention would lose one of its important features.

Depending upon the low temperatures which it is anticipated may be encountered, various amounts of calcium chloride may be incorporated with the water. Similarly the quantity of the colloid which is incorporated may vary not only with the salt content but with the maximum temperature expected to be encountered and with the type of coal. It is of importance to compound our coating in such a way that it be easy flowing at the moment of application, even at temperatures substantially below the freezing point of water, since highly viscous or pasty masses will form heavy deposits, which are not only uneconomical but will attract and attach to the coal foreign dust particles, as derived, for instance, from the railroad locomotive during transit. Our composition is designed merely to keep the coal itself from dusting, and not to clear the surrounding atmosphere from dust. Dust picked up from the air by heavy pasty coatings mar the luster of the coal, and such coatings also render the coal slimy to the touch. As a typical example of our composition, the following formula, because of its efficiency and low cost, has been found satisfactory under varying conditions.

Calcium chloride 100 lbs.
Cornstarch (containing preferably 6% glutin) 8 lbs.
Water 50 gallons

In making this composition, a paste is first made from the entire amount of starch with about 1 gallon of water. This paste is then stirred into about fourteen gallons of water. Or, the starch may be stirred at once into fifteen gallons of water, and stirring continued until all lumps have disappeared and a uniform suspension of the starch has been achieved. Under continued agitation, the calcium chloride is added. The dissolution heat of the latter is sufficient to swell the starch and bring it into colloidal solution to produce a thick shiny liquid which is stirred for another ten minutes. Then the remainder of the water is added.

In spite of the calcium chloride content, this composition exhibits remarkable anti-corrosive properties, which must be ascribed to the presence of the starch. In order to get some definite information about this, four carefully measured and

weighed steel plates, 1/8 inch in thickness, were immersed in equal volumes of—

(1) plain water,
(2) applicants' composition as described above and containing starch in a highly purified condition,
(3) applicants' composition made with starch having a glutin content of approximately 6%, and
(4) a straight calcium chloride (without starch) solution containing the salt in an amount corresponding to that in applicants' composition.

These test solutions with immersed steel plates were allowed to stand side by side in the laboratory at a temperature varying between 70 and 80 degrees Fahrenheit. All solutions were kept in covered glass beakers to guard against rapid evaporation of water. From time to time, the steel plates were removed, carefully washed, dried and weighed. Losses in weight were recorded and calculated into percent loss per square inch of steel plate. It was found that water and the straight calcium chloride solution corroded the steel at a much higher rate than did either one of applicants' compositions. As compared with water, applicants' composition containing starch in its pure form reduced the rate of corrosion by 87.9%, while under the same conditions the composition containing glutinous starch reduced it by 97.2%. As compared to the straight calcium chloride solution, the reductions are 87.5% and 97.1%. These figures were calculated from the losses per square inch of exposed surface of steel plates measuring 2 x 2 x 1/8 inches after 32 days of immersion. In water the loss amounted to 0.0574% per square inch, in the calcium chloride solution 0.0556% per square inch, in applicants' composition made with pure starch 0.00695% per square inch, and that with glutinous starch 0.00162% per square inch. Not only do these figures demonstrate the remarkable corrosion inhibiting quality of starch, but also the added advantage gained by using a starch containing about 6% natural glutin. The practical value of this is obvious. It eliminates the serious trouble characteristic to the straight salt treatments explained above, and in fact, while applicants' solution has been used for more than one year to treat several million tons of coal, no evidence of corrosion can be seen anywhere in the vicinity of the sprays, or on the mining or railroad equipment.

The corrosion inhibiting effect of the colloid in applicants' solution is apparent even with highly diluted calcium chloride solutions. Comparative corrosion tests were carried out in exactly the same manner described above but with a 0.4% watery calcium chloride solution and a solution of applicants' wherein the calcium chloride content was reduced to 0.4% of the water employed but the regular amount of pure starch was present. These tests revealed that steel plates immersed in the former for 33 days suffered a loss in weight amounting to 0.0841% per square inch of surface, while in the latter the loss amounted only to 0.0094% per square inch of surface. In other words, the starch reduced corrosion by approximately 89%.

Applicants' preferred solution is slightly milky in appearance, and transparent in thin layers. Its viscosity ranges between 18 and 19.5 sec. Saybolt furol at 70 degrees Fahrenheit. This viscosity changes but very slightly with changing temperatures, including those below zero. No difficulties are therefore encountered while spraying in severe winter weather.

Applicants' solution is odorless, and does not acquire any odor when kept for a long time.

Particles of coal coated with this composition will not freeze solidly together at temperatures as low as —10 to —20 degrees Fahrenheit. At very low temperatures, the coating material may form some ice but in doing so the remaining liquid will become more concentrated and its freezing point will be substantially below that of the original composition. In other words, the coal will not freeze solidly together because the coating remains mushy long after the initial freezing point has been reached. Moreover, it has been observed on several occasions, that coal treated with applicants' composition is not penetrated by the cold as quickly as untreated coal, indicating that the coating must have some insulating properties. Even though the coating may be partially frozen, the remaining liquid and the film-forming agent, i. e., the starch, maintain the coal dustless, black and glossy.

The coating will not dry out entirely even at temperatures ordinarily encountered in summer because under such conditions, the colloid of the composition will set into a semi-gelatinous film which will not only assist the salt to retain an excess of moisture but will exert influences of its own toward the retention of moisture. This semi-gelatinous film impregnated with a substantially liquid form of a crystalloid, is, once formed, extremely resistant to the action of water, as for instance rain, in which it will swell but not again dissolve, and it also holds the impregnating crystalloid with great tenacity. In other words, the coating formed by our composition is initially a liquid sprayable without the aid of heat throughout the temperature range ordinarily encountered in summer or winter, and remains liquid or semi-liquid on the coal throughout said range of temperature.

Different sizes of coal and different types of coal from different locations require different quantities of coating solution depending both on the degree of concentration of the solution and on the surface area of the coal fragments to be coated. Thus the large sizes will usually require less per ton than slack coal, for instance. Furthermore, a certain size coal coming from one field may require but half the amount necessary to treat satisfactorily the same size coal mined in another field. In general, if the solution is applied in such concentrations and at such rates that from about one pound to about eight pounds of crystallizable and colloidal solids combined are deposited, per ton of coal treated, the results will be entirely satisfactory. In no case is it necessary, or desirable, to apply such amounts in treatment that the coal appears to be wet or soaked to the saturation point. Thus an initially dry coal might require only one and one-half gallons to be satisfactorily treated for dust, although it might require six or more gallons to reach that point of saturation where any amount of additional solution applied, will run off immediately.

However, the cost of the treatment, the necessity of maintaining the combustion qualities of the coal substantially unimpaired and the fact that the treatment must not appreciably affect either the ash content of the coal or the fusion point of the ash, are factors which largely, if not entirely, control the ranges within which the ingredients of our composition may be employed. Hence, when the commercial aspects of the in-

vention are given due consideration, it will be found that practical operations are confined to depositing rather small quantities of solids on the coal, as set forth above.

Likewise, factors other than the ones mentioned require that the deposits on the coal be not only small but that the character of the composition be of such limpid consistency that it may be applied to form on the coal an extremely thin coating or film at any temperature ordinarily encountered.

It is one of the objects of applicants' invention to provide a composition which upon application to natural, irregular, loose particles of coal forms thereon a liquid, or upon partial drying, a semi-gelatinous film of such strength that the fine dust particles present at the moment of application are attached to the main and larger particles, but not strong enough to injure the free-running quality of slack coals by the formation of lumps or to induce caking of the coal in railroad cars or furnaces.

For example, the formula given above produces a liquid composition of the desired characteristics. The quantity of the colloid (cornstarch) therein is 8% by weight of the salt (calcium chloride); the quantity of salt is two pounds per gallon of water; and the quantity of colloid is only 0.16 pound per gallon of water. In other words, the amount of salt is twelve and one-half times that of the colloid employed.

In any case, the maximum quantity of calcium chloride or its equivalent will probably not exceed about six pounds per gallon of water or fall materially below one pound per gallon. Similarly, starch or other colloids between the limits of about one-tenth of a pound and about one-quarter of a pound per gallon of water will probably meet all practical needs. However, it is to be understood that the ingredients are so proportioned that the composition is a free-flowing liquid solution at temperatures substantially below 32 degrees Fahrenheit, and substantially maintains this characteristic at the lowest temperatures expected to be encountered by the coal.

One of the outstanding features of our treatment is that it renders the coal clean in the sense that the coal will not substantially blacken surfaces with which it comes in contact. For example, it may be handled without blackening the hands and, as compared with untreated coal which leaves a black stain when subjected to the following test, a teacupful poured on a piece of newspaper and then poured off by tilting the paper, leaves no stain whatsoever on the paper.

Another of the outstanding features of our invention is that our treatment will reduce degradation. There are three factors which influence the degradation of coal, disintegration caused by water freezing within the pores, oxidation of pyritic sulfur with subsequent hydration and expansion of the formed ferrous sulphate, and rough handling.

The anti-freezing properties of our composition eliminate the first cause entirely. Degradation by oxidation of pyritic sulfur is especially pronounced during dry storage of coal. One of the reaction products, ferrous sulphate attracts water vigorously and binds it in the form of crystal water, thereby expanding considerably. As this process takes place beneath the surface of the coal within its pores, this expansion will cause shattering or degradation. However, if sufficient moisture is present, the ferrous sulphate will leach out rather than expand within the coal. Consequently, degradation will not occur or be reduced to a minimum. Our invention provides a coating which keeps the coal sufficiently moist all the time, so that leaching of the iron salt may take place and degradation be reduced in the manner aforesaid.

Our coating apparently increases the surface strength of coal, thereby minimizing degradation caused by rough handling. This at least is our explanation of a fact established not only by the behavior of treated coal in silos, storage piles, etc., but also by actual laboratory tests. For instance, buckwheat coal was sifted to remove oversize and undersize particles. Half of this coal was treated with our composition, the other half left untreated. Both were run through an approved stoker and the degradation in size measured by sifting and weighing the coal. The results demonstrated that even under these severe conditions, where the coal is subject to forces of a higher order than under ordinary handling, as loading and unloading, our treatment reduced degradation by more than 15%. In commercial practice, as substantiated by observation, the reduction is much greater, for the treatment exerts its protecting influence against all of the cited factors causing or furthering degradation such as freezing, chemical reaction and mechanical handling.

Combustion tests have also shown that our treatment reduces the formation of fly-ash by more than 32%.

If coal treated with our composition is drenched with water, it will give up entrained moisture about twice as fast as untreated coal wetted in the same manner. This is probably caused by the semi-gelatinous surface film which prevents undesirable excess moisture from penetrating and thus allows dripping and evaporation to a desirable equilibrium to take place faster. This feature is regarded as an outstanding advantage by men in the coal industry, and the conclusion can be drawn that coal treated with our composition rids itself quickly of excess moisture disadvantageous to combustion but retains tenaciously such small amounts of water as are known to favor and improve combustion.

Another desirable feature of our invention is the following. If certain types of coal, Illinois coal for instance, are stored for even a short length of time, a white efflorescence appears thereon. Coal of such inferior color value or rank is hard to sell, but if coated with our composition will show no efflorescence long after efflorescence has appeared on untreated coal of the same type.

Another, and quite unexpected feature, is that, by subjecting coal to our treatment, the danger of spontaneous combustion if not permanently eliminated is at least removed for a very substantial period of time. Coal dealers who have been handling coal treated with our composition for more than one year have experienced no trouble whatsoever in this respect.

What we claim is:

1. An aqueous liquid composition for treating coal in the form of free-flowing, separate, irregular particles or fragments to render it clean and dustless and to prevent it from substantially discoloring objects with which it comes in contact, said composition comprising water and dissolved therein a hygroscopic, non-deliquescent organic colloid capable of forming a gel with water in amount from about 0.10 to about 0.25 pound per gallon of water and a water-soluble, crystallizable salt adapted to lower substantially the

freezing point of water in amount from about 1 to about 6 pounds per gallon of water, said composition being characterized by the fact that it is free-flowing and is readily sprayable at a temperature below 32° F. and by the fact that it is substantially non-corrosive with respect to metal equipment used in coal handling.

2. An aqueous liquid composition for treating coal in the form of free-flowing, separate, irregular particles or fragments to render it clean and dustless and to prevent it from substantially discoloring objects with which it comes in contact, said composition comprising water and dissolved therein a hygroscopic, non-deliquescent organic colloid capable of forming a gel with water in amount of about 0.16 pound per gallon of water and a water-soluble, crystallizable salt adapted to lower substantially the freezing point of water in amount of about 2 pounds per gallon of water, said composition being characterized by the fact that it is free-flowing and is readily sprayable at a temperature below 32° F. and by the fact that it is substantially non-corrosive with respect to metal equipment used in coal handling.

3. An aqueous liquid composition for treating coal in the form of free-flowing, separate, irregular particles or fragments to render it clean and dustless and to prevent it from substantially discoloring objects with which it comes in contact, said composition comprising water and dissolved therein starch in amount from about 0.10 to about 0.25 pound per gallon of water and a water-soluble, crystallizable salt adapted to lower substantially the freezing point of water in amount from about 1 to about 6 pounds per gallon of water, said composition being characterized by the fact that it is free-flowing and is readily sprayable at a temperature below 32° F. and by the fact that it is substantially non-corrosive with respect to metal equipment used in coal handling.

4. An aqueous liquid composition for treating coal in the form of free-flowing, separate, irregular particles or fragments to render it clean and dustless and to prevent it from substantially discoloring objects with which it comes in contact, said composition comprising water and dissolved therein starch in amount of about 0.16 pound per gallon of water and a water-soluble, crystallizable salt adapted to lower substantially the freezing point of water in amount of about 2 pounds per gallon of water, said composition being characterized by the fact that it is free-flowing and is readily sprayable at a temperature below 32° F. and by the fact that it is substantially non-corrosive with respect to metal equipment used in coal handling.

5. An aqueous liquid composition for treating coal in the form of free-flowing, separate, irregular particles or fragments to render it clean and dustless and to prevent it from substantially discoloring objects with which it comes in contact, said composition comprising water and dissolved therein cornstarch in amount of about 0.16 pound per gallon of water and calcium chloride in amount of about 2 pounds per gallon of water, said composition being characterized by the fact that it is free-flowing and is readily sprayable at a temperature below 32° F. and by the fact that it is substantially non-corrosive with respect to metal equipment used in coal handling.

6. The method of treating natural coal in the form of separate, irregular free-flowing particles and fragments to render it clean, dustless and resistant to freezing and to prevent it from substantially discoloring objects with which it comes in contact, which comprises spraying upon the separate, irrgular, free-flowing particles and fragments of natural coal a free-flowing, substantially non-corrosive composition resistant to freezing at a temperature below 32° F. and which comprises water and dissolved therein a hygroscopic, non-deliquescent organic colloid capable of forming a gel with water in amount from about 0.10 to about 0.25 pound per gallon of water and a water-soluble, crystallizable salt adapted to lower substantially the freezing point of water in amount from about 1 to about 6 pounds per gallon of water and permitting the said composition to remain in contact with the coal.

7. The method of treating natural coal in the form of separate, irregular, free-flowing particles and fragments to render it clean, dustless and resistant to freezing and to prevent it from substantially discoloring objects with which it comes in contact, which comprises spraying upon the separate, irregular, free-flowing particles and fragments of natural coal a free-flowing, substantially non-corrosive composition resistant to freezing at a temperature below 32° F. and which comprises water and dissolved therein starch in amount of about 0.16 pound per gallon of water and calcium chloride in amount of about 2 pounds per gallon of water, and permitting the said composition to remain in contact with the coal.

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