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MEANS FOR MARKING GRANULAR, LUMPY, AND DUSTY COMMODITIES

Raymond E. Miskelly, Plymouth, Mass., assignor to Plymouth Cordage Company, Plymouth, Mass., a corporation of Massachusetts

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This invention relates to means for marking granular, lumpy and dusty commodities.

The invention is suitable for marking bituminous coal and other carbonaceous solid fuel, as coke, anthracite and briquettes; also commodities of a different nature, for example, crushed ore, or stone, or grain, or seed; and any other whose physical structure and commercial status are such as to warrant the use of the mark herein described for distinguishing the origin, the ownership, the kind, grade or quality, the age, or some other characteristic of the particular aggregation of nodular, fragmented or comminuted particles to which the mark is applied.

It is one object of the invention to provide a mark which will live as a mark as long as the commodity lives to which it is applied, yet which need not be a thing that interferes with the normal appearance of the commodity, or its utility, as by discoloring, defacing or adulterating it. As applied to such a friable commodity as coal, this stated object means that the mark is to survive the normal tumbling, crushing, abrasion, oxidation and other experiences which coal undergoes during shipment, handling and storage with incidental lapse of time, exposure to air and to weather; and with superficial flaking and fragmentation such as occurs as coal dries.

Toward these ends the invention provides a dispersion of a finely divided substance whose particles constitute a mark in that they shine out as bright points of light, especially in a dim light or darkness.

Dispersed in the commodity which they mark, they do not change the appearance of that commodity as seen in ordinary light. And they may be themselves substantially invisible. But when ultraviolet rays are thrown upon a mass of that commodity they glow with distinctive brilliance.

In dusty commodities, as bituminous coal, the marking particles may be independent of the coal lumps; that is, they do not need lumps to receive and support them, because they may be particles of dust mixed in the coal dust. In a commodity having but little dust, as briquettes, or anthracite, where the lumps or other units are all so large that a marking dust might settle and fail to maintain its dispersion, the marking particles may be held on the units of the marked commodity. In either case the mark is a dispersion of particles of an extraneous substance such that the particles fluoresce so as to glow brightly in the dark, under ultraviolet rays; and these particles may be carried by dispersed particles of a second extraneous substance. In optimum form for bituminous coal the mark has the property that the activating particles, which may be particles or products of a suitable dye, are adsorbed on or otherwise carried by the second mentioned dispersed extraneous substance, which may be of cellulosic nature, as wood or cotton. Or, the carrier particles may be a colorless lacquer, or may be of other substance, as, for example, an inorganic powder, or fragments of wool. It is not necessary that the fluorescing particles be visible in ordinary light after being dispersed. And the second mentioned extraneous substance, the carrier, may be one that ultimately becomes unnoticeable in the commodity, as, for example, either by itself adhering on the surface of a lump without showing color, or by reason of adhesion of coal dust to its own surface.

It has been previously proposed to mark coal by coating the lumps with some color or material so as to change the appearance of the coal, or by distributing manufactured geometrical shapes of wood. The success of the coloring depends upon there being lumps of sufficient size, or else requires much color material. Geometrical shapes are expensive to make. And neither system is applicable to grain or seed. The present invention can be used with any of such commodities; its shapes are not geometrical but may be fragments of waste material—inexpensive, and yet of distinctive type; and it is not dependent on there being lumps in the commodity, but it can be effective in dust. However, the marker can be held on lumps, either by use of an adhesive, or by adsorptive affinity of the carrier particles, or in some cases by affinity of the marking particles alone.

One instance of a carrier made of material extraneous to the commodity is finely divided wood, such as sawdust, or wood flour, or chopped particles of excelsior. The selection of marking material can be made among substances for which wood has a strong adsorbent affinity with incidental property of fluorescence. Examples are found in dyes. The concentration of fluorescent power on each particle of wood may be so strong that whatever of coal dust gathers on the particle does not occlude all the light that shines forth when ultraviolet rays are applied.

If the commodity which is to be marked has sizable lumps or nodules, such as the customary lumps of bituminous coal, or those found in anthracite, or coke, or briquettes, a substance to fluoresce for the marking may be selected from among those which are fluorescent in powder form and for which the marked commodity has a retentive affinity, for example, as coal has for commercial anthracene. In such case the marker may be dusted over the commodity, for its particles to cling on the lumps or nodules by mutual

affinity and surface adhesion. When finely dispersed in small percentage in coal, these particles will be substantially invisible in ordinary light, yet will shine out in brilliance under ultraviolet rays in which the coal is dark. If the marking powder which it is desired to employ is one for which the retentive affinity of the commodity is low, a liquid adhesive carrier for holding the particles of marker on the lumps may be employed, as starch or gum arabic, or an insoluble glue as casein. An example of a marking powder, whose density makes it desirable that an adhesive be employed for holding it in dispersion, is any fluorescing variety of zinc sulfide.

When a liquid is employed to carry the marker, the spraying of the liquid upon a thin passing stream of the commodity, as upon coal descending a chute, disperses globules. These adhere, and, upon drying, the marking material they carry is fixed in its dispersion through the mass of the commodity. An example of a liquid carrier, for which the solids of a lump commodity have high adsorptive or other retentive affinity, is lacquer. Applied to coal, their mutuality of affinity spreads the globules into films. They are detectible only upon very close inspection of the coal. The usual flaking which occurs with the drying of the coal does not prevent any particle, whether on a lump or in the dust, from glowing in the darkness of ultraviolet rays.

The color of fluorescent glow may be pre-selected by observing the color in which the energy, applied through ultraviolet rays, is re-emitted by the particular kind of material. A diversity of marks, among which selection can be made, can also be had by predetermining various densities of dispersion, for applying the carrier particles throughout the coal which they are to mark. One way to do this is to combine in a mass the output of a chute whose product is marked with that of one or more whose output is not marked. Diversity can also be had by choosing the carrier particles from materials having diverse characteristics, the peculiarities which characterize any particular mark being discernible by examination of the individual particle, perhaps under the microscope, after such a particle has been found in the coal by its emission of light. An example, in wood, is the diversity of characteristic shapes which exists between shreds of sawdust and choppings of excelsior; or between sawdust of one particular kind of wood and the dust of another particular kind of wood having different natural cell structure. The invention thus serves an important industrial need, in that it enlarges the field from which marks are available for selection, to distinguish individually the products of different mines, or different companies, or other sources, as compared with the limitations of choice which are at present imposed by the smallness of variety available in systems now in use.

It is another feature that the mark of the invention can be utilized without its introducing anything deleterious. Wood fragments are always combustible with the coal; and so are lacquers. In the case of grain, wood fragments will be removed with the hulls in the operation of milling. In either case the quantity introduced is not sufficient to constitute an adulteration, since the dispersal of only a pound or so of sawdust through each ton of coal gives an effective frequency of points of light.

It is convenient herein to use the term "particles" in referring to the fluorescent substance, i. e., the marking material, which "activates" the "base" material whose small solids or liquid globules are also "particles" that "carry" the marking material. If the carrier is a soluble liquid or solid, this carrier may be the solute in a volatile solvent by which the dispersal is effected, but from which the solvent will later evaporate, leaving the carrier holding the mark in the dispersed relation. Thus a nitrocellulose lacquer, or a less inflammable lacquer as cellulose acetate, or one that is less expensive as shellac, may be a base to be activated into capacity for fluorescing by carrying a suitable dye; and may itself be dissolved in a volatile solvent, and in that solvent be sprayed in globular particles which become dispersed throughout the mass of the granular commodity which they ultimately mark. And it is convenient to use the term "granular" to signify all the various kinds and grades of granular, nodular, lumpy, dusty, or powdery commodities.

For practicing the invention by admixture of particles of wood or the like the said particles may be of any predetermined shape, definite or nondescript; but economy will dictate their being made in quantity by mechanism. Hence those made by any particular kind of operation, as by sawing, will have certain characteristics in common, and these characteristics will be identifiable by ordinary inspection or test. For a particular marking the base material may be selected wholly of a single variety; or may be a selected mixture of varieties. The range available for selection of this base material is infinite in number of varities. Economical and convenient base material is found in the sawdust which is a waste product in lumber mills; but other bits of wood are available, or may be produced by cutting or chipping processes; and other durable materials are available, whose nature is cellulosic so that they are adsorbent of the activating material, among which are paper, paper pulp, rayon and cotton—which can be used either as cut fibre or short lengths of yarn or thread; also bast fibres, as those of flax, jute and other grasses; and also leaf fibres as those of sisal; and products of numerous other plants, also animal products, as wool, hair, silk—any of which can be fragmented to desired specified dimensions—as well as synthetic products of all sorts.

A preliminary bleaching of the base material, as with sodium hydrosulfite, sometimes helps the brilliance with which the particles fluoresce after the activating material has been applied. This is especially true of resinous wood such as pine; while fragments of other woods, as of some poplar, are satisfactory without it.

The substance which is to constitute the active marking particles is to be selected among those which fluoresce brightly when dispersed in the coal or other commodity which is to be marked. Against a black background of coal, a dull fluorescence is not a satisfactory mark, as compared with one that shines forth brilliantly. Selection can be made only on a basis of discovery by experiments with the substance proposed, for some substances do not fluoresce brightly, although other similar substances do. Some are fluorescent in one solution and not in another solution. Some may be normally fluorescent, and yet not appear so when dispersed in coal; and, by contrast, Diazo Fast Yellow 2G does not fluoresce in water solution, yet does in solid form; and does so when it is carried on cellulosic material, as wood sawdust. Some are fluorescent when in a certain solvent, but when dyed on cellulose are not so; and certain substances are found to fluo-

resce satisfactorily when taken in their commercial or technical form, as available in the market, but not when chemically pure. The active particles herein described therefore are those which in a practical sense glow luminously in their surroundings when exposed to ultraviolet rays, the mark being best seen when the main body of the mass which is marked is examined in shadow or in light which provides only poor visibility.

Numerous substances exist which meet the requirements for the marker of the invention. I have found that activating materials suitable for application to a solid base such as sawdust or other cellulosic material by usual dyeing methods include the following dyes, having names recognized in the trade as follows:

Dye	Color index number	Color and reaction of activated material (carrier) under ultraviolet rays
Acriflavine	#790	Yellow.
Thioflavine TG Ex	#815	Yellow to greenish yellow.
Eosin OJ	#768–#771	Red.
Phosphine GN	#793	Yellow.
Phosphine 2RN	#793	Orange.
Erie Flavine S	#816	Yellow.
Thiazine Red RXX	#225	Rose.
Nacelan Pink G	None	Orange.
Celliton Brilliant Yellow FF	do	Yellow.
Brilliant Dianil Green G	do	Green.
Calcocid Fluorescent Blue G	do	Blue.
Alcosol Golden-Yellow IGK	do	Olive.
Rhodamine B Extra	#749	Orange.
Primuline	#812	Yellow.
Auramine O	#655	Do.
Diazo Fast Yellow 2G	#654	Bluish-white.
Rhodamine 6GDN	#752	Orange.
Pyronine	#741	Blue.
Anthracene (Tech.) 1% sol. in benzene (base for dyes).		Yellowish-green.

Among dyes heaving a community of physical and chemical characteristics such that each might be expected to meet the requirements of the invention, I have found many inoperative but have demonstrated that the foregoing are operative.

In each case in which there are corresponding dyes of the same color index number but produced by another maker and called by a somewhat different name, the result and behaviour have been found similar to those above listed; and these are considered equivalents. The Color Index numbers are those given in the Color Index of the Society of Dyers and Colorists, edited by F. M. Rowe.

The foregoing table represents reaction of activated material wherein the concentration of dyes used is 0.5% based on the weight of material treated; ratio of material to water 1:30; dyed at 180° F. for 15 minutes, except Auramine O at 140°.

In the foregoing list, primuline is most satisfactory and is the substance preferred for activating sawdust for yellow fluorescence. In case the sawdust is of wood whose results are improved with a preliminary bleaching, primuline is not affected by a hydrosulfite bleach, and the bleaching and dyeing can take place in the same bath, with a saving in cost.

A preferred way to apply the activating material to a base such as sawdust which will become its carrier is either by spraying the fluorescent activating material in volatile solution over a mass of the sawdust, or by immersing the sawdust in such a solution, so that the dust becomes thoroughly wetted; then spreading the sawdust, and drying it by evaporation of the volatile vehicle. Activating material then remains in the sawdust adsorbed or otherwise retained on the wood. Care should be taken that the wood particles are loose from each other, so that when applied to the granular commodity they can easily become widely dispersed through it. Ordinarily the drying will put them into condition for this, but if necessary the mass of activated sawdust or other fragmented material may be agitated or beaten to make its particles be separate from each other. The base material thus activated is then to be applied distributively to the body of coal, or whatever other granular mass is to be marked.

Each of these steps can conveniently be executed by a continuous process, in which fresh supplies of the material or commodity concerned move continuously forward, in any of a variety of ways which will naturally occur to the engineer in charge. For example, a stream of the activated loose particles may be scattered so that the particles fall freely through air over and upon a thin layer of coal which is sliding and tumbling downward as a stream along an inclined chute.

If the activated particles are to be dispersed in a liquid, as in a solution of lacquer or a resin, natural or synthetic, in a volatile solvent, the activator may be applied to a body of the liquid by a mixing process, producing a suspension or a solution of the activator in the carrier, or, in the case of lacquer, an actual dyeing of the lacquer; and a solution of the carrier in the volatile solvent; and then the liquid may be sprayed upon such a thin tumbling layer of the commodity.

The following are examples of dyes for treating a liquid base such as lacquer or shellac in the practice of the invention so that when sprayed on the commodity, as coal, the reaction of the deposited particles under ultraviolet rays will be as indicated, demonstrated operative among numerous similar that are found not satisfactory:

Dye	Color index number	Reaction under ultraviolet
Celliton Yellow FF	None	Yellow.
Auramine O	655	Do.
Primuline Base		Do.
Rhodamine B	749	Orange.
Rhodamine 6GDN	752	Do.

In some cases, in which anthracene is an example, a fluorescent powdered solid has retentive affinity for coal, and may be applied to this commodity by being merely dusted over a passing stream of the commodity. But fluorescent pigment can be had, such as fluorescent zinc sulfide, or other powder which is independently fluorescent, as ground fluorescent lake, dispersed and held on granules of commodity by an adhesive. If the dispersion of particles should chance to be discernible in ordinary light, no harm is done, but the marking effect is that which is seen under ultraviolet rays. An example of such a lake is one made from aluminum sulfate, sodium silicate and a suitable yellow dye such as primuline. For holding on the commodity a pigment which does not naturally adhere, as for holding anthracene on briquettes or anthracite, or for holding a lake, starch or gum arabic can be applied in liquid form to the commodity with or previous to the application of the particles that are to constitute the mark.

The coal or other commodity thus marked may then go along in its usual course in commerce, carrying with it the mark. If the mark and the carrier are selected of inconspicuous materials.

or if they pick up coal dust, the mark will not affect the appearance of the coal, and the presence of the mark may be not noticeable. But the mark will be discernible at any time, and preeminently so in darkness, by a casting of ultraviolet rays upon a sample taken from the mass. Sources of ultraviolet rays are available in portable form, using filters to eliminate visible light.

The mark thus made can indicate whatever those who use it may elect that the mark shall mean. For example, authenticity of the marked coal as having come from a particular source can thus be told, ascertained, or verified. If all of the coal produced in a particular locality is thus marked distinctively, absence of the mark in a particular body of coal found in the market will show that the origin of this coal was elsewhere. Presence of the mark in abnormal scarcity will indicate that coal of other origin has been admixed. This provides a safeguard against unscrupulous dealers, who may introduce coal other than a particular kind ordered; also it provides a means of learning the source, in case of doubt. The ease and low cost at which the sawdust, or other activated fragmented base, can be dispersed through the coal at the breaker, prevents the counterfeiting of the mark by anyone who is a mere dealer; for no mere dealer is in position to counterfeit the mark by making a good distribution through his coal, except at a cost which would more than exhaust all profits he might hope to make by his proposed fraudulent substitution.

The materials for the carrier, and those for the activating, are of such low cost, and the cost of applying the activating material to the commodity is so low, that the retail price of the commodity is not unduly burdened by the applying of the mark. The reaction of the mark to ultraviolet rays, by shooting forth points of light, is distinctive; and it demonstrates convincingly the authenticity of the body of coal in which it is found. This is in contrast to the difficulty sometimes experienced in distinguishing the mark, if any, under methods of marking which rely upon changing the appearance of the coal. Other features of utility are the ubiquity of these points of light in a mass of coal, viewed in darkness; and the great number of varieties, distinguishable from each other, in which the mark of the invention can be practiced on coal and other commodities without injuring the commodity or adding appreciably to its price.

It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty exist in the invention disclosed.

I claim as my invention:

1. In combination, bulk coal and an identifying marking material therefor, said identifying marking material being combined with and dispersed throughout said bulk coal, said identifying marking material comprising a fluorescent substance and a carrier therefor, said carrier being of a kind of material which is extraneous to said coal and consists of water-insoluble, discrete, solid particles, said fluorescent substance and carrier being blended with said bulk coal in such a manner as to be inconspicuous in ordinary light and having the property that in their dispersion throughout said bulk coal they alter the appearance of the bulk coal by fluorescence of the fluorescent substance when the bulk coal is subjected to ultraviolet rays.

2. The combination as set forth in claim 1 wherein said identifying marking material is loosely dispersed throughout to said bulk coal.

3. In combination, bulk coal and an identifying marking material therefor, said identifying marking material being combined with and dispersed throughout said coal, said identifying marking material comprising a fluorescent substance and a carrier therefor, said carrier being in the form of water-insoluble, discrete, solid particles which are extraneous to both said fluorescent substance and said coal, said fluorescent substance and carrier being blended with said bulk coal in such a manner as to be inconspicuous in ordinary light and having the property that in their dispersion throughout said bulk coal they alter the appearance of the bulk coal by fluorescence of the fluorescent substance when the bulk coal is subjected to ultraviolet rays.

4. The combination as set forth in claim 1 wherein said carrier for said fluorescent substance adheres to said coal.

5. In combination, bulk coal and an identifying marking material therefor, said identifying marking material being combined with and loosely dispersed throughout said bulk coal, said identifying marking material comprising a fluorescent substance and a carrier therefor, said carrier being individual particles of fragmented cellulosic material, said fluorescent substance and said fragmented cellulosic material being blended with said bulk coal in such a manner as to be inconspicuous in ordinary light and having the property that in their dispersion throughout said bulk coal they alter the appearance of the bulk coal by fluorescence of the fluorescent substance when said bulk coal is subjected to ultraviolet rays.

6. In combination, bulk coal and an identifying marking material therefor, said identifying marking material being combined with and loosely dispersed throughout said bulk coal, said identifying marking material comprising a fluorescent substance and a carrier therefor, said carrier comprising fragmented wood, said fluorescent substance and said fragmented wood being blended with said bulk coal in such a manner as to be inconspicuous in ordinary light and having the property that in their dispersion throughout said bulk coal they alter the appearance of the bulk coal by fluorescence of the fluorescent substance when the bulk coal is subjected to ultraviolet rays.

7. The combination as set forth in claim 5 wherein the fluorescing substance is primuline.

8. In combination, bulk coal and an identifying marking material therefor, said identifying marking material being combined with and dispersed throughout said coal, said identifying marking material comprising a fluorescent substance and a carrier therefor, said carrier comprising dried particles of lacquer, said fluorescent substance and said individual particles of lacquer being blended with said bulk coal in such a manner as to be inconspicuous in ordinary light and having the property that in their dispersion throughout said bulk coal they alter the appearance of the bulk coal by fluorescence of the fluorescent substance when the bulk coal is subjected to ultraviolet rays.

9. The combination as set forth in claim 8 wherein the carrier is shellac.

RAYMOND E. MISKELLY.