

# UNITED STATES PATENT OFFICE

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## SIMULTANEOUS BLUEING AND DUSTPROOFING OF SOLID CARBONIFEROUS FUELS

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This invention relates to oil-in-water emulsions comprising a dustproofing oil and ultramarine, to the application of these emulsions to solid carboniferous fuels in particulate form, and to such fuels which have been treated with said emulsions.

Hereinafter said fuels, which include bituminous coal, anthracite coal, bituminous coke, and briquetted fuels comprising these fuels or mixtures thereof, will be generically referred to as "coal."

In the past a demand has arisen for a "blue coal," that is, coal which when viewed en gros by the ordinary consumer under ordinary conditions has a blue appearance or "mass tone." At the present time the color blue has acquired a "secondary meaning" and is a very valuable trade-mark.

The problem of blueing coal was solved from the optical point of view by U. S. Patents 2,129,901 and 2,129,902, which disclosed a process for depositing a brilliantly blue ferro-ferricyanide salt on the coal. This process, however, required relatively costly chemicals, and careful and continuous technical control both of the chemicals and of the coal.

To solve the problem of costs it was proposed to pigment coal directly with the bright blue ultramarine pigment of commerce. When this pigment was applied to coal, however, it washed off readily when sprayed with water. Subsequently, the discovery was made by Dieterle (U. S. 2,323,748/9) that ultramarine could be coated with a water-insoluble soap or with a free organic acid, that this ultramarine could be dispersed in water, and that when this ultramarine was sprayed on coal, it was transformed irreversibly into an adherent blue pigmentation which was water-repellent and which completely met the specifications of the trade. The Dieterle process of coloring coal is amazingly cheap and efficient. Only a few ounces of ultramarine are needed to pigment a ton of coal, and the process is conducted almost automatically by common labor without the use of any special or costly equipment.

Since the war the greatly increased price of anthracite coal, bituminous coal, and coke, coupled with sharp consumer preference for oil and natural gas, has made further improvements in the characteristics of these solid fuels imperative.

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At the present time two of the most disadvantageous characteristics which coal possesses are (1) it freezes into a solid mass when wetted and then subjected to sub-freezing temperatures, thereby increasing handling costs; and (2) it develops large volumes of dust when shot into the coal bin of the average consumer, thereby increasing the work of the average housewife. A demand, therefore, has arisen for a coal which is free from these characteristics.

It has long been and still is the general practice of coal retailers to drench coal with a heavy spray of water immediately prior to delivery of the coal to the ultimate consumer. While this spraying diminishes the tendency of the coal to raise clouds of dust when shot into the householder's bin, the effectiveness of this water treatment disappears in a few hours and thereafter the coal dusts just as readily as if it had not been wetted. This practice of wetting down the coal is particularly objectionable in that a large amount of water drains from the coal and collects in pools on the householder's cellar floor.

In recent years, both of the above-noted disadvantageous characteristics of ordinary coal, that is, coal which has not been blueed, have been largely overcome by applying dustproofing oily liquids, hereinafter called "dustproofing oils." Application of these oils at once permits the fuel to shed rain water, and dustproofs the fuel as well.

When such dustproofing oils were applied to coal pigmented with ultramarine, however, the blue coloration of the coal instantly and substantially completely disappeared. As ultramarine has about the same index of refraction as that of the oils employed, this oiling caused the ultramarine to lose its surface reflectivity and to assume an apparently black glossy color which was indistinguishable from the color of the coal. As a result, the valuable "secondary meaning" of the blue coloration was completely lost.

This masking or destruction of the tinctorial value of the ultramarine occurred regardless of whether the dustproofing oil was applied to the fuel before or after application of the ultramarine, and regardless of whether the oil was applied as such, or as an aqueous emulsion.

The surprising discovery has now been made that when ultramarine is added to an emulsion of a dustproofing oil of the oil-in-water type,

prepared as set forth below, and when an emulsion of this type is sprayed on coal, the emulsion breaks in such a way that the oil and a portion of the ultramarine part company and that as a result sufficient ultramarine having its brilliantly blue "dry shade" becomes visible on the surface of the coal to impart a blue mass tone to the coal. It has been found that after the emulsion has broken and after the water contained in the emulsion has run from the thus pigmented coal, the coal has a generally dust-proof and water repellent surface.

The above-described discovery as to the manner in which the emulsions of the present invention break could not have been predicted because when sprayed on ordinary steel test panels, these emulsions yield a substantially continuous film of oil having a grimy appearance in which the color of the ultramarine is virtually completely masked.

This discovery could not have been predicted for the further reason that it would have been expected that the ultramarine would run off with the water. Ultramarine is an organophobic, hydrophilic pigment which has a selective affinity for water and which is normally readily wet thereby.

The reason for this behavior of the ultramarine emulsion is not known, and it is not intended to limit the present invention to any particular theory of action.

More in detail, according to the present invention, an emulsion is made by dispersing a water-soluble organic anionic or non-ionic emulsifying agent, a dustproofing oil, and ultramarine with at least sufficient water to form an oil-in-water emulsion. This emulsion is then sprayed on coal. It is immaterial from the point of view of result as to how this emulsion is formed and the constituents may be added in any sequence to the water.

Additional pigments may be added to the emulsions of the present invention to vary the color thereof. For example, addition of chrome yellow will give an emulsion having a greenish tint.

As emulsifying agent a preformed soap may be used. However, it is preferred to form the soap in situ by reaction of a solution of a predetermined amount of a water-insoluble, soap-forming organic acid and a saponifying agent. This agent or base may be the hydroxide, carbonate or bicarbonate of sodium, potassium or ammonium, or morpholine, triethanolamine, triethylamine, tetramethyl ammonium hydroxide or piperidine, as is well-known in the art. The acid may be any of the ordinary cheap soap-forming acids such as oleic, palmitic, stearic or tall oil fatty acids. In addition, undecylenic acid, coconut oil fatty acids, castor oil fatty acids, soya oil fatty acids, abietic acid, naphthenic acids, perilla oil fatty acids, and neatsfoot oil fatty acids may be used in proportional amounts. I prefer to use the cheapest acids, and for this purpose tall oil acids, oleic acid and stearic acid have been found very suitable. The proportion of the soap-forming acid should be sufficient that when this acid is saponified, the oil and the ultramarine are emulsified with only slow stirring. An amount of acid ranging from 3% to 20% of the weight of the oil and of the ultramarine is usually sufficient for this purpose. I prefer to use about 4% to 9%. With this proportion, the emulsion begins to separate within a few minutes when stirring is halted, a thin layer of oil forming on the surface, and this is desirable.

It is surprising that the proportion of the

saponifying base added is not critical. When less is added than the amount necessary to convert all the acid to the soap, the unreacted acid simply dissolves in and becomes part of the oil phase. For example, when 15% of acid is added based on the weight of the ultramarine and dustproofing oil and only sufficient saponifying agent is added to saponify  $\frac{2}{3}$  of said acid, the balance of the acid dissolves in the dustproofing oil and does not produce any harmful effect. When more than the stoichiometrical proportion of base is added, the excess serves to stabilize the emulsion. Since the soap-forming acids are usually more expensive than the dustproofing oils I prefer to add a substantial excess of the base, which excess may be two hundred or three hundred percent. I prefer to add about 275 percent of the stoichiometrical proportion of the base, particularly when the emulsion is to be applied in freezing weather.

This invention is not limited to the use of soap as a dispersing agent. Any other of the numerous anionic or non-ionic dispersing agents for emulsifying dustproofing oils may be used, as is well-known in the art. Among these are: alkyl benzene sodium sulfonate (UltraWet 30E), sodium lignin sulfonate, a naphthalene sulfonic acid-formaldehyde condensation product (Tanak L), an alkylated aryl polyether alcohol (Triton N-100), a polyethylene ether of a long chain fatty acid (Emulfor ON), soda ash and distilled tall oil (Acintol D). The first five require vigorous agitation and therefore are not preferred. The last mentioned agent, however, gives excellent results with slow stirring. Anionic dispersing agents are preferred, and cationic emulsifying agents should be avoided.

In any event, sufficient emulsifying agent should be present to permit formation of an emulsion which is apparently stable on slow stirring and which forms a thin film of oil within two minutes when stirring is halted.

It is a very surprising advantage of the present invention that a satisfactorily adherent pigmentation results when ordinary, untreated, commercial ultramarine is used. This discovery was unexpected because when a water dispersion of ordinary, untreated ultramarine is sprayed on coal, the deposited ultramarine washes off readily after drying, and the Dieterle ultramarine, described above, was produced to overcome this high lack of permanence. No soap insolubilizing agent or acid is present in the instant process, and it therefore could not have been predicted that when ordinary ultramarine is emulsified as set forth below, the ultramarine acquires a sufficient degree of adhesiveness necessary for practical commercial use. The reason for this remarkable improvement is not known.

It is an additional surprising feature of the present invention that Dieterle's ultramarines may also be used. It could not have been predicted that these Dieterle ultramarines would not be preferentially wet by the dustproofing oils, or that the tinctorial value of the Dieterle ultramarines would not be masked by the dustproofing oil.

The ratio of water to the soap, the dustproofing oil, and the blue pigment should be ample to insure formation of a blue, perfectly fluid oil-in-water emulsion, which begins to break when allowed to stand for two minutes. Preferably the weight of the water is about 500% of the weight of the materials therein. When this proportion of water is used, the emulsion breaks rapidly on the coal, and excess of water does no harm. If

this proportion of water is reduced by more than 50% uneconomically thick deposits of ultramarine will result, and pronounced masking of the color of the pigment will again become apparent. This materially increases the cost of attaining satisfactory pigmentation without producing any corresponding advantage, as it is only necessary that the weight of the ultramarine on the coal be not less than about 0.00005 and not more than about 0.00025 of the weight of the coal.

This invention is not limited to any particular dustproofing oil. It is a surprising advantage of the present invention that under the conditions employed herein ultramarine remains unwetted by these diverse examples of which are oils, cyclic hydrocarbons including hydrocarbon naphthenic oils, straight chain hydrocarbon oils including diesel oil, automotive lubricating oils, oily aryl esters including dibutyl and the lower alkyl phthalates, and vegetable oils, such as linseed oil and cottonseed oil have an index of refraction which is nearly the same as that of ultramarine (1.55). The index of refraction of most of these oils is within the range 1.35-1.6, and some oils have indices of refraction as high as 1.75. They do not freeze under ordinary winter conditions and have a very low rate of volatilization. The preferred oil is Acme Oil B, a straw-colored, very fluid hydrocarbon naphthenic oil boiling above 200° C. and having a specific gravity of 0.900. Its index of refraction is about 1.5 at 25° C. Not more than about 1.5 parts by weight of oil should be used per part of ultramarine. Substantially increasing the proportion of oil dims the final blue coloration, and use of a lesser proportion of oil merely yields a coal of reduced anti-dusting properties. Good results are obtained when 1.0-1.4 parts of dustproofing oil are used per part of ultramarine.

It is advantageous to wash the coal before it is sprayed with the emulsions of the instant invention to prewet the surface of the coal and to wash the dust therefrom, but it is an advantage that it is not necessary to do so.

In commercial utilization the emulsion is continuously sprayed over the coal as it enters the cars or trucks for shipment at a predetermined rate such that the coal, when dry, has a blue mass tone. Generally, this rate is between about 0.1 and 0.5 lb. and preferably 0.4 lb. of ultramarine per ton of coal. When the percentage of dustproofing oil in the emulsion is high as compared with the percentage of ultramarine, the weight of ultramarine per ton of coal should also be high. Substantially all the oil and ultramarine are retained by the coal as it dries, and a relatively clear solution of water, containing some of the emulsifying agent and any excess soda ash, drips from the cars.

Immediately upon completion of the spraying, the coal has a black and glossy appearance. It acquires a metallic blue coloration fairly rapidly, and the bright blue, "dry" shade of the ultramarine does not begin to appear for an hour or more. Development of maximum blue coloration throughout the entire mass of the coal takes about twenty-four hours and often longer, depending on weather conditions. This delay is not disadvantageous because ordinarily the coal is in transit for several days before it reaches the householder.

When examined individually, the several lumps of coal are always seen to be unevenly pigmented. In nearly every instance the maximum amount

of visible blue is found on the surfaces which were horizontal during the drying period. This is particularly noticeable in the case of anthracite coal, which has numerous broad, glassy facets. With anthracite, maximum coloration is usually found on the crevices which were horizontal during the drying period. A blue of lesser or metallic brilliance is found on the broad planes and very little blue is precipitated on the more sharply inclined facets. Distinct coloration, however, may be exhibited even by the latter facets. The oil tends to collect on the lower surfaces of the particles of the fuel.

Throughout the entire mass, certain of the lumps of the coal appear to be nearly completely uncolored. This is not disadvantageous because sufficient blue is present in other lumps to give the entire mass its characteristic blue appearance.

Bituminous coal and coke have very irregular surfaces and are free from the broad, glassy facets characteristic of anthracite coal. As a result, the vertical surfaces of these two fuels are usually more easily colored, which often makes possible a slight reduction in the proportion of ultramarine which must be present to "blue" these fuels.

It is frequently desired to apply the emulsions of the present invention during freezing weather, and for this purpose the emulsions which contain a large percentage of soda ash are preferred.

The following examples illustrate preferred embodiments of the invention and are not in limitation thereof. Parts are by weight unless otherwise noted.

#### Example 1

Ten parts of soda ash are dissolved in 900 parts of water, and 15 parts of red oil (oleic acid) are dissolved in 100 parts of Acme Oil B (Atlantic Refining Co.), a straw-colored, very fluid, high boiling, cyclized hydrocarbon of the naphthenic type having a specific gravity of 0.900 and an index of refraction of about 1.4965. The oil is then stirred into the soda ash solution. An emulsion forms immediately which persists with only slight stirring. To this emulsion are added 72 parts of untreated ordinary ultramarine blue. With continued stirring, a bright blue emulsion results which begins to break within two minutes when allowed to stand. This emulsion when sprayed on washed anthracite coal, bituminous coal and bituminous coke at the rate of 0.4 lb. of ultramarine per ton of fuel, forms a distinctively blue product of markedly reduced dusting characteristics. The visible ultramarine appears to be concentrated in the crevices. After two to four hours, when viewed from a distance, the coal is seen to have a blue mass tone. The blue is not noticeably washed off by the fall of heavy rain.

#### Example 2

Example 1 is repeated, the ultramarine, however, being added to the soda ash solution. An emulsion results which has the same properties as the emulsion of Example 1.

#### Example 3

Example 1 is repeated, the ultramarine, however, being added to the oil-oleic acid mixture. An emulsion results which has the same properties as the emulsion of Example 1.

## Examples 4-9

The procedure of Example 1 is repeated using however, the following proportions of the materials. In each instance 1000 parts of water is used.

Example	Soda Ash	Oil	Acid		Ultra-marine
			Name	Parts	
4.....	1.5	15	Oleic.....	2.2	15
5.....	11.2	112	do.....	16.7	80
6.....	3.4	112	do.....	8.0	80
7.....	11.2	112	Tall oil F. A.....	16.7	80
8.....	11.2	112	Stearic.....	16.7	80
9.....	11.2	112	Abietic.....	16.7	80

<sup>1</sup> Acme Oil B.

Emulsions result which have substantially the same properties as the emulsion of Example 1. Satisfactory blueing occurs when these emulsions are sprayed on coal at the rate of 0.4 lb. of ultramarine.

## Examples 10-14

The procedure of Example 1 was followed in which, however, the Acme Oil B was replaced with an equal weight of the following oils:

Example	Oil
10.....	Hydrocarbon automotive engine oil SAE 40.
11.....	Hydrocarbon automotive engine oil SAE 59.
12.....	Dibutyl phthalate.
13.....	Raw linseed oil.
14.....	Nujol.

## Example 15

The procedure of Example 1 is followed using however an oleic acid coated ultramarine prepared according to the example of Dieterle U. S. 2,323,749. A similar emulsion results. When this emulsion is sprayed on coal, a pigmentation is obtained which is similar to that obtained by Example 1 of the instant application and which is somewhat more rain-resistant.

## Example 16

Example 15 is repeated using however a sodium oleate coated ultramarine prepared according to Example 1 of Dieterle U. S. 2,323,748. A similar result is obtained.

## Example 17

Example 15 is repeated using however an aluminum oleate coated ultramarine according to Example 1 of Dieterle U. S. 2,323,748 from which the excess aluminum sulfate has been extracted. A similar result is obtained.

I claim:

1. A process for the simultaneous "blueing" and dustproofing of a solid carboniferous fuel

which comprises forming an oil-in-water emulsion from an ultramarine, a water-insoluble oil having an index of refraction between 1.35 and 1.75, a water-dispersible emulsifying agent selected from the group of anionic and non-ionic emulsifying agents, and water, said oil being in the dispersed phase and said ultramarine being in the continuous phase of said emulsion, and spraying said fuel with said emulsion at a predetermined rate to deposit on said fuel a quantity of ultramarine amounting to at least 0.00005 of the weight of said fuel, the weight of said oil in said emulsion being not greater than about 150% of the weight of said ultramarine and the weight of said water in said emulsion being at least about 250% of the weight of the other constituents of said emulsion, and said emulsion being characterized by an instability which results in phase separation upon standing.

2. A process according to claim 1 wherein the fuel is anthracite coal.

3. A process according to claim 2 wherein the dust-proofing oil is a cyclized hydrocarbon naphthenic dustproofing oil having an index of refraction of about 1.5 and a specific gravity of about 0.9.

4. A process according to claim 3 wherein the emulsifying agent is the sodium soap of talloil fatty acids.

5. A process according to claim 4 wherein the weight of water is about 500% of the weight of the other constituents of the emulsion.

6. A process according to claim 5 wherein the weight of the oil is about 1.0 to 1.4 of the weight of the ultramarine.

7. A process according to claim 6 wherein the emulsion is sprayed upon the fuel at the rate of about 0.4 lb. of ultramarine per ton of fuel.

8. A process according to claim 1 wherein the fuel is bituminous coal.

9. A process according to claim 8 wherein the dustproofing oil is a cyclized hydrocarbon naphthenic dustproofing oil having an index of refraction of about 1.5 and a specific gravity of about 0.9.

10. A process according to claim 9 wherein the emulsifying agent is the sodium soap of talloil fatty acids.

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The following references are of record in the file of this patent:

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