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**Method and composition for reducing the strength of ice.**

57

This invention is directed to the reduction of the strength of ice in association with solid particulate materials, such as, for example, coal, by applying to the solid particulate material, prior to exposure to water freezing conditions, a composition comprising a mixture of a hydrocarbon liquid and an ethoxylated aliphatic primary or secondary alcohol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof. The composition may also contain an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or propylene oxide and containing from 1 to 3 oxyalkylene units.

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BACKGROUND OF THE INVENTION

~~This invention is directed to reducing the~~  
strength of adhesion of solid particulate materials  
obtained under freezing conditions by ice formation  
between particles. In particular, this invention is  
5 directed to the addition to the surface of solid inorganic  
particulate materials of a composition which causes  
weakening and collapsing of inter-particulate ice bonds  
that form in the material, such weakening and collapsing  
occurring in many cases when a stress is applied, typically  
10 from the weight of a mass of the particles. In particular,  
this invention is specially adapted to the treatment of  
particulate coal to enhance its bulk handling character-  
istics under low temperature (i.e., freezing) conditions.

There is described in the literature the use of  
15 a number of compositions for reducing the interbonding  
effect of ice formation between particulate materials.

U.S. Patent 3,794,472, for example, describes  
that coal particles are prevented from freezing together  
and/or to the surfaces of coal storage containers by coating  
20 either the coal particles and/or the surfaces of said stor-  
age containers with a thin film of a composition comprising  
a hydrocarbon liquid which has emulsified therewith from 5  
to 75% by weight of an aqueous solution of a polyhydric  
alcohol.

25 The sole formulation in the patent is described  
as containing the following ingredients: 50 percent by  
weight of Fuel oil - #2 Diesel, 24 percent by weight of  
ethylene glycol, 24 percent by weight of water and 2 per-  
cent by weight of an emulsifier which is a 50:50 weight

blend of nonylphenol reacted with 9 moles of ethylene-oxide and pentaerythritol etherified with oleic acid.

However, at low temperatures such an emulsion has a tendency to separate into a water and an oil phase  
5 and thus become ineffective.

Additionally, a commercially available formulation for treating coal particles to prevent them from freezing together contains the following ingredients:  
65 weight percent of fuel oil and 35 weight percent of  
10 dialkyl phenol ethoxylate.

However, such a formulation is unsuitable since the dialkyl phenol ethoxylate is not biodegradable and thus, remains in the environment.

Thus a need exists for a formulation for treating  
15 solid particulate materials to reduce the strength of adhesion under freezing conditions which does not contain water and a nonbiodegradable material.

The composition of this invention does not contain water but does contain a biodegradable material.

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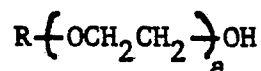
#### THE INVENTION

This invention is directed to compositions for the treatment of particulate matter subjectable to water freezing conditions which comprises a mixture of a hydrocarbon liquid which has a solidification or pour point  
25 not greater than <sup>-18 °C</sup> ~~0°F~~ and an ethoxylated primary or secondary aliphatic alcohol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof.  
The composition may additionally contain an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or  
30 propylene oxide and containing from 1 to 3 oxyalkylene units.

The hydrocarbon liquid suitable for use in this invention is selected from one or more liquid aliphatic, aromatic and/or naphthenic hydrocarbons which have a solidification or pour point at not greater than 0°F.

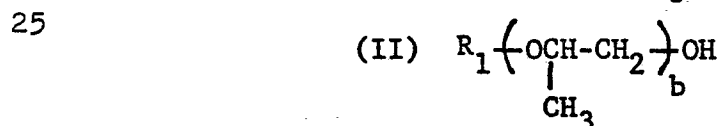
5 These liquids include No. 2 fuel oil, diesel oil, kerosene, turbo fuel, and the like. Mixtures of hydrocarbon liquids may also be used.

The ethoxylated aliphatic primary or secondary alcohol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof is of the following formula:



wherein R is an alkyl radical of 7 to 20 carbon atoms and  
15 a is an integer of from 1 to 7. Preferably, the ethoxylated alcohol is a secondary alcohol wherein R is alkyl of 11 to 15 carbon atoms and a is 3. Mixtures of ethoxylated aliphatic alcohols may also be used.

The composition of this invention may also contain  
20 an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or propylene oxide and containing from 1 to 3 oxyalkylene units and is selected from one or more compounds of the following formulae:



wherein R<sub>1</sub> is alkyl containing from 1 to 6 carbon atoms, and b is an integer of from 1 to 3.

30 The preferred alkyl ether of a glycol is ethylene

glycol ethylether and has the following formula:

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ . This ether is commercially available under the designation Cellosolve<sup>®</sup> Solvent (sold by Union Carbide Corporation).

5           The mixture of this invention contains from about 30 to about 95, preferably from about 55 to about 85 weight percent of hydrocarbon liquid; from about 5 to about 50, preferably from about 10 to about 30 weight percent of the ethoxylated aliphatic alcohol, and when  
10 used, from about 3 to about 20, preferably from about 5 to about 15 weight percent of the oil soluble alkyl aryl ether.

          The amount of the composition of this invention which is typically supplied to the inorganic mass is about  
15 3.0 weight percent, typically about 1.0 weight percent based upon moisture content in the inorganic particulate mass being treated. Larger amounts can be employed but they are not ordinarily required. The amount to use can be determined by measuring the moisture content of the inor-  
20 ganic particulate mass (see e.g., ASTM D-3302-74) and supplying to that mass, in an uniform matter, the composition of this invention in the amount which test data shows to provide the desired amount of fragileness (or brittleness) to the particulate mass when brought to a frozen state.

25           Various methods may be used to supply the compositions of this invention to the particulate mass. Standard treating procedures employed in the art for spraying a liquid uniformly onto a particulate mass may be employed. For example, the composition may be sprayed across a zone  
30 through which a stream of the particles to be treated is

passed. A particular illustration of this would be to place an annular tube above a hopper car that is being loaded with the particulate mass. The tube contains a multiplicity of spray heads aimed at the interior area circumscribed by the tube and the tube acts as a manifold for the solution fed to the spray heads. The solution of the composition is fed to the tube at a rate to supply the desired amount of the composition on the particulate mass to be treated. The mass of particulates are fed through the tube into the hopper car. Another technique involves spraying the top of a mass of the particles and allowing the composition to drain through the mass to cover particles at the bottom as well.

Another technique involves dropping the particles onto a trough which feeds the particles to a hopper car or to a storage facility. While the particles run down the trough they are sprayed with a solution of the composition of this invention.

#### EXAMPLES

The following examples serve to give specific illustrations of the practice of this invention but they are not intended in any way to limit the scope of this invention.

#### PREPARATION AND TESTING OF PACKED COAL SPECIMENS

The effect of moisture content on the compressive strength of frozen particulate masses of coal was demonstrated. The coal employed was 3/8 inch (passed 3/8 inch mesh; 0.9525 cm mesh) Eastern bituminous type coal.

A 350 gram sample of the dry coal is placed in a one-liter beaker. The moisture content of the coal is

adjusted to 8 percent by the addition of 30.4 grams of water. The prepared treating solution is applied dropwise uniformly across the sample surface with a laboratory syringe and is blended with a spatula until solution and coal  
5 appear uniformly mixed. The moistened coal is quickly placed in a mold (to prevent evaporation losses) and a 13.635-pound steel weight (6,185 grams) having an outside diameter of <sup>61 mm</sup>~~2.40 inches~~ is inserted into the top of the mold and allowed to compress the sample. The weighted,  
10 coal-filled mold is then placed on a laboratory shaker and vibrated for one minute. The 6,185 gram weight is designed to simulate the compressive forces exerted on the bottom of a coal car by an eight-foot high column of coal <sup>1.917 N/cm<sup>2</sup></sup>~~(2.778 psi)~~.

15 The top of each container is sealed with aluminum foil to prevent moisture loss. Each specimen is then conditioned at room temperature for about four hours to complete the equilibration of moisture and test fluid on the coal. It is then placed in a mechanical freezer  
20 operating at <sup>-12.5 ± 1 °C</sup>~~-10 ± 2 °F~~ for 18-24 hours.

(The mold is a cylinder fabricated from split 2 1/2 inch (63.5 mm) inside diameter aluminum tubing which is 6.0 inches (152.4 mm) high. The bottom is sealed with an aluminum plug fitted with an "O" ring and the longitu-  
25 dinal seams are made moisture-tight by applying a thin film of a nonhardening gasket sealer. The mold's inner surfaces are coated with a mold release agent (such as a noninterfering silicon or teflon-based material) and the entire assembly is held together with two standard <sup>76 mm</sup>~~3-inch~~  
30 diameter worm drive hose clamps.)

A specimen is removed from the freezer and quickly but gently opened and separated from the frozen coal. The

compressive strength of the coal is promptly determined using an Instron Model TTC physical testing machine. The specimen is placed between parallel stainless steel platens connected to the Instron's 10,000 pound (4,500 kg) load cell, and the plates are closed by an electric drive at a constant rate of 2.5 inches (6.35 cm) per minute. The pounds force required to crush the specimen is recorded. The crushing force is converted to pounds per square inch (psi), i.e., the crushing stress by dividing it by 4.909 square inches, the cross sectional area of the specimen, according to the following equation:

$$\text{Crushing stress (psi)} = \frac{\text{Crushing force (pounds)}}{4.909 \text{ (in.}^2\text{)}}$$

15

#### Control A

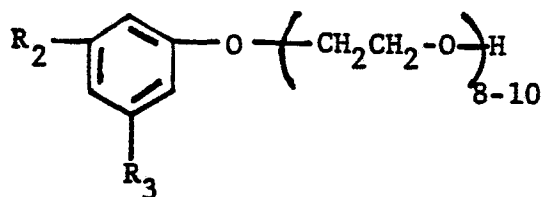
Kerosene was added in amounts of 0.198 milliliters (equivalent to one pint/ton of coal), 0.396 milliliters (equivalent to two pints/ton of coal), and 0.595 milliliters (equivalent to three pints/ton of coal) to the mold containing coal and treated and tested as described in the Preparation and Testing of Packed Coal Specimens, supra.

The crushing stress is set forth in the Table. The numerical value of the crushing stress is the average of the number of specimens tested, and is set forth in the Table. The Table also shows the percent reduction of the crushing stress of the treating material as compared to that of untreated coal (containing 8 percent water and prepared as described in the Preparation and Testing of Packed Coal Specimens, supra), which is <sup>175.8 N/cm<sup>2</sup></sup>~~254.8 psi~~ (based on the average of 86 specimens tested).



### Control B

The procedure of Control A was exactly repeated except that the treating solution was a commercially available material (manufactured by Nalco Chemical Corporation under the trademark Nalcoal 8894) of a mixture of 65 percent kerosene and 35 percent of dialkyl phenol ethoxylate of the following formula:

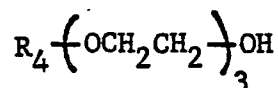


wherein  $\text{R}_2$  and  $\text{R}_3$  are alkyl groups.

The results are shown in the Table.

### Example 1

The procedure of Control A was exactly repeated except that the treating solution was a mixture of 80 percent kerosene and 20 percent of an ethoxylated alcohol of the following formula:



wherein  $\text{R}_4$  is 11 to 15 carbon atoms.

The results are shown in the Table.

### Example 2

The procedure of Control A was exactly repeated except that the treating solution contained the following:

70 percent kerosene,

10 percent  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ , and

20 percent  $\text{R}_4 - \left( \text{OCH}_2\text{CH}_2 \right)_3 \text{OH}$

wherein  $R_4$  is 11 to 15 carbon atoms.

The results are shown in the Table.

The data in the Table show that the compositions  
of this invention are effective in reducing the strength  
5 of ice in association with coal.

TABLE

| <u>Example</u> | <u>0.198 ml.of Treating Solution</u> |                                               |                                        | <u>0.396 ml.of Treating Solution</u> |                                               |                                        | <u>0.595 ml.of Treating Solution</u> |                                               |                                        |
|----------------|--------------------------------------|-----------------------------------------------|----------------------------------------|--------------------------------------|-----------------------------------------------|----------------------------------------|--------------------------------------|-----------------------------------------------|----------------------------------------|
|                | No.of<br>specimens<br>tested         | Crushing<br>stress<br>(psi) N/cm <sup>2</sup> | Reduction of<br>crushing stress<br>(%) | No.of<br>specimens<br>tested         | Crushing<br>stress<br>(psi) N/cm <sup>2</sup> | Reduction of<br>crushing stress<br>(%) | No.of<br>specimens<br>tested         | Crushing<br>stress<br>(psi) N/cm <sup>2</sup> | Reduction of<br>crushing stress<br>(%) |
| Control A      | 10                                   | (255) 176                                     | 0                                      | 12                                   | (233) 161                                     | 8.7                                    | 12                                   | (218) 150                                     | 14.5                                   |
| Control B      | 36                                   | (228) 157                                     | 10.6                                   | 36                                   | (181) 125                                     | 29.0                                   | 36                                   | (164) 113                                     | 35.8                                   |
| 1              | 13                                   | (193) 133                                     | 24.3                                   | 16                                   | (167) 115                                     | 34.3                                   | 16                                   | (159) 110                                     | 37.5                                   |
| 2              | 35                                   | (178) 123                                     | 29.9                                   | 36                                   | (182) 126                                     | 28.4                                   | 36                                   | (148) 102                                     | 41.5                                   |

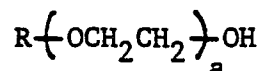
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WHAT IS CLAIMED IS:

1. A composition for the treatment of particulate matter subjectable to water freezing conditions which comprises a mixture of a hydrocarbon liquid which has a solidification or pour point not greater than ~~0°F~~ <sup>-18°C</sup> and an ethoxylated aliphatic primary or secondary alcohol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof.

2. A composition as defined in claim 1, wherein the hydrocarbon liquid is selected from No. 2 fuel oil, diesel oil, kerosene or turbo fuel.

3. A composition as defined in claim 1, wherein the ethoxylated alcohol is of the following formula:

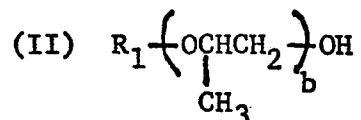
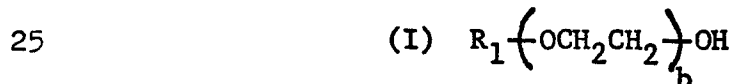


wherein R is an alkyl radical of 7 to 20 carbon atoms and a is an integer of from 1 to 7.

4. A composition as defined in claim 3, wherein R is an alkyl radical of 11 to 15 carbon atoms and a is 3.

5. A composition as defined in claim 1, which contains an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or propylene oxide and containing from 1 to 3 oxyalkylene units.

6. A composition as defined in claim 5, wherein the alkyl ether is selected from one or more compounds of the following formulae:



wherein  $R_1$  is alkyl containing from 1 to 6 carbon atoms and b is an integer of from 1 to 3.

7. A composition as defined in claim 6, wherein the alkyl ether has the following formula:



8. A composition as defined in claim 1 which contains from about 30 to about 95 weight percent of the hydrocarbon liquid.

9. A composition as defined in claim 1 which  
10 contains from about 5 to about 50 weight percent of the ethoxylated aliphatic alcohol.

10. A composition as defined in claim 5 which contains from about 3 to about 20 weight percent of the oil soluble alkyl ether.

15 11. A composition as defined in claim 1 which contains from about 55 to about 85 weight percent of a hydrocarbon fluid selected from No. 2 fuel oil, diesel oil, kerosene, or turbo fuel, from about 5 to about 50 weight percent of an ethoxylated aliphatic primary or  
20 secondary alcohol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof, and from about 5 to about 15 weight percent of an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or propylene oxide and containing from 1 to 3 oxyalkylene units.

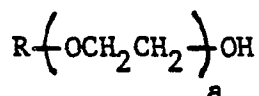
25 12. The process of treating inorganic particulate materials which comprises supplying to the surface of such particulate materials a small quantity of a composition comprising a solution of a mixture of a hydrocarbon liquid which has a solidification or pour point not greater than  
-18 °C

30 ~~0°F~~ and an ethoxylated aliphatic primary or secondary alco-

hol containing 1 to 7 oxyethylene units and 7 to 20 carbon atoms in the alkyl portion thereof.

13. A composition as defined in claim 12 wherein the hydrocarbon liquid is selected from No. 2 fuel oil,  
5 diesel oil, kerosene or turbo fuel.

14. A composition as defined in claim 12 wherein the ethoxylated alcohol is of the following formula:

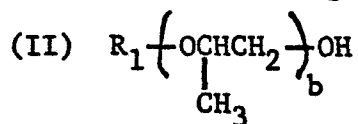
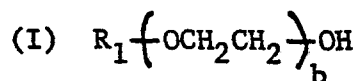


10 wherein R is an alkyl radical of 7 to 20 carbon atoms and a is an integer of from 1 to 7.

15. A composition as defined in claim 14 wherein R is an alkyl radical of 11 to 15 carbon atoms and a is 3.

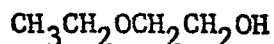
16. A composition as defined in claim 12, which  
15 contains an oil soluble alkyl ether of a glycol derived from ethylene oxide and/or propylene oxide and containing from 1 to 3 oxyalkylene units.

17. A composition as defined in claim 16, wherein the alkyl ether is selected from one or more compounds of  
20 the following formulae:



wherein  $R_1$  is alkyl containing from 1 to 6 carbon atoms and b is an integer of from 1 to 3.

25 18. A composition as defined in claim 17, wherein the alkyl ether has the following formula:



19. A composition as defined in claim 12 which contains from about 30 to about 95 weight percent of the hydrocarbon liquid.

20. A composition as defined in claim 12 which  
5 contains from about 5 to about 50 weight percent of the ethoxylated aliphatic alcohol.

21. A composition as defined in claim 16 which contains from about 3 to about 20 weight percent of the oil soluble alkyl ether.