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CREOSOTE COMPOSITION OF IMPROVED FLOWABILITY AND ITS PRODUCTION

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This invention relates to high-boiling hydrocarbon mixtures of improved flow characteristics. In one specific aspect, it relates to creosote, rendered capable of flowing at lower temperatures, which is more easily handled during commercial use. In another aspect, it relates to a method of treating creosote to make it readily dischargeable from tank cars and other shipping containers.

Creosote is a distillate of coal tar produced by the high temperature carbonization of bituminous coal. It is a mixture of high-boiling hydrocarbons comprising about 90 percent aromatic compounds having 1–4 fused rings, about 5 percent phenolic compounds, about 3 percent nitrogenous heterocyclic compounds and 2 percent sulfur-containing hydrocarbons. Commercial grade creosote, which is used extensively as a wood preservative, has a continuous boiling range between about 200 and 355° C.; generally not more than 5 percent is distillable at 210° C. and not more than 85 percent or less than 60 percent is distillable at 355° C.

Creosote is normally liquid at temperatures of about 40° C. At lower temperatures, the higher boiling constituents crystallize out and the creosote becomes a partially solidified mass. When crystal formation occurs, it is difficult to redissolve the crystals; to do so it is necessary to heat the creosote at high temperatures for a prolonged period of time.

In commercial practice creosote is shipped to the consumer in tank cars equipped with built-in steam coils in order to provide the necessary heat to liquify crystallized creosote and to effect discharge thereof. Creosote is usually charged to the tank car at a temperature of about 75° C. Because of the temperature drop encountered (particularly in cold weather) when creosote is shipped over long distances, it arrives at its destination in a more or less solid state. In order to discharge completely the creosote from the shipping car, it is generally necessary to heat the creosote to a temperature of about 75–80° C. for about 10–12 hours or more. Since creosote consumers are reluctant, because of the cost of steam involved, to heat the creosote to that temperature for the length of time required to remove it, large volumes of creosote remain in the car and are returned to the shipping point. This inefficient operation results in considerable monetary loss occasioned by the loss of revenue from the returned creosote, the transportation costs to and from the customer and the expense of cleaning the tank car.

Quite surprisingly, we have discovered a method of treating creosote whereby the flow temperature, i.e. the temperature to which creosote must be heated to obtain sufficient dissolution of the crystals to permit complete discharge from a tank car or container, is reduced approximately 15–30° C. and the required heating time is reduced to the extent of about 50 percent.

It is, therefore, an object of the present invention to provide creosote capable of flowing or being discharged from containers at a reduced temperature and in a shorter period of time. It is a further object to provide a method of treating creosote to render it easily dischargeable from tank cars or other containers without adversely affecting the preservative properties of the creosote.

In accordance with the invention, creosote is intimately admixed with about 0.001–0.1 percent by weight, based on the weight of the creosote, of a water-soluble polyoxyalkylene condensate, the condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a 1 percent by weight solution of the condensate in water.

The polyoxyalkylene condensate useful in the invention is made by condensing ethylene oxide, propylene oxide, or mixtures thereof to form a high molecular weight ether containing the group $-(C_nH_{2n}O)_mOH$, wherein n is an integer having a value of 2 or 3 and m is a large whole number. The alkylene oxide may be condensed solely with itself or the polyether chain may be built upon another organic compound such as an amine. While there are many commercially available types of such condensates, only those which are water-soluble and which have a very high molecular weight are useful in the present invention. We have found that the most suitable way of determining whether a particular condensate is effective is by measuring the viscosity of a one percent by weight solution of the condensate in water at 25° C. The viscosity measurement provides a relative indication of the molecular weight of the condensate. Only those condensates which are characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a freshly made one percent solution of the condensate in water are suitable in the invention. A particularly useful polyoxyalkylene condensate is sold by the Union Carbide & Chemical Company under the trade name "Polyox Coagulant." "Polyox Coagulant" is a water-soluble, solid polyethylene oxide condensate having an estimated molecular weight of between about 1 and 10 million and a softening point of 65–67° C. A one percent water solution of "Polyox Coagulant" has a viscosity of 5,500 centipoises and higher at 25° C.

The amount of polyoxyalkylene condensate admixed with the creosote must be carefully controlled. If insufficient condensate is admixed therewith, the creosote will not flow at reduced temperatures. If too large a quantity of condensate is used, it tends to cause gelation of the creosote, thus defeating the purpose of the invention. Generally, the condensate is admixed with creosote in an amount of about 0.001 and 0.1 percent by weight, based on the weight of the creosote. With most creosotes, if more than about 0.1 percent is used, there is a definite tendency toward gelation. However, if the creosote contains a minimum amount of the very high boiling constituents, the condensate may be used in greater amounts without gel formation and the beneficial effect of the invention is still obtained. Preferably, the amount of condensate in the final creosote ranges between about 0.003 and 0.01 percent by weight.

In accordance with the method of the invention, the condensate is added to creosote in sufficient amount as an aqueous solution containing between about 0.3 and 3 percent by weight condensate. If the water solution contains more than about 3 percent by weight condensate,

it becomes extremely viscous and is difficult to admix uniformly with the creosote. The lower limit of condensate concentration in the aqueous solution is governed by practical, rather than theoretical, considerations. If the aqueous solution is too dilute large quantities of water must be added to the creosote to obtain the desired concentrations of condensate therein. The specifications for commercial creosote require that it contain less than about 3 percent by weight water. The condensate is added in aqueous solution, since it is difficult to obtain a uniform admixture when solid condensate is used.

The condensate is added to the creosote at a temperature between the temperature at which the creosote is incipiently liquid and the boiling point of the aqueous solution of condensate. Generally, this temperature ranges between 40 and 95° C. Since it is commercial practice to charge the creosote to a tank car or shipping container at a temperature of about 75° C., it is convenient to add the aqueous solution of the condensate during the charging operation. Mixing can be accomplished by pumping the condensate solution into the creosote feed line leading to the tank car. The creosote in the tank car is agitated with air to provide an intimate admixture.

Our invention is further illustrated by the following examples:

EXAMPLE I

The following test procedure was established to determine the effectiveness of the condensate in improving the flow properties of creosote:

The creosote under test is heated to approximately 80° C. and a measured amount is weighed in a 250 ml. beaker. The desired amount of condensate-water solution of required concentration is added thereto and the mixture is agitated with a laboratory mixer for five minutes. After agitation, the treated mixture is poured into a graduated cylinder. An untreated portion of the creosote is also poured into a graduated cylinder as a control. After at least 20 hours at a given temperature, each cylinder is inverted and its contents are decanted into a beaker. The amount of material decanted from each cylinder is noted and recorded. If the creosote does not flow from the graduate at the temperature selected, the graduate and its contents are placed in a water bath maintained at an elevated temperature. After a fixed heating period, the decanting procedure is repeated and the temperature is recorded. The amount of material flowing from the graduate is again noted and recorded. If the creosote does not flow at the second temperature, the heating and decanting procedure is repeated at higher temperatures until all of the material flows from the graduate.

Samples of creosote were treated by adding thereto measured quantities of the polyethylene oxide condensate sold commercially as "Polyox Coagulant." As we have noted hereabove, "Polyox Coagulant" is a high molecular weight water-soluble white resin melting at 65–67° C. A 1 percent by weight solution of this material in water has a viscosity of 5,500 centipoises and higher at 25° C. as measured by Brookfield viscometer RVF at 2 r.p.m. using a No. 2 spindle. The samples contained varying amounts of condensate and were tested at different temperatures The flow properties of each of the treated creosotes were compared with those of an untreated sample. The results are shown hereunder in Table I.

Table I

Type of Creosote	Concentration of Condensate in Creosote, percent by weight	Concentration of Water in Creosote, percent by volume	Test Temperature, ° C.	Decantation, percent by volume
Commercial	0.033	2.3	25	90
Do	0.000	1.3	25	0
Commercial—Laboratory Redistilled	0.0033	1	25	97
Do	0.0000	0	25	5
Do	0.01	3	6	95
Do	0.00	0	6	5
Commercial—Laboratory Redistilled + 10 percent creosote crystals	0.0033	1	25	0
Do	0.0000	0	25	0
Do	0.0033	1	35	100
Do	0.0000	0	35	10

It is observed from the data of Table I that creosote, when treated according to the method of the invention, has remarkably improved flow properties. The creosote used during the tests was modified to provide for variations ordinarily incurred in commercial production. The creosote designated as "Commercial" contained a higher percentage of high-boiling aromatic materials than did the laboratory redistilled creosote. The data show that treated laboratory redistilled creosote could be substantially removed from its container at a temperature as low as 6° C., a result which did not obtain with the corresponding untreated creosote. The creosote containing 10 percent creosote crystals, which is representative of a commercial creosote having a high percentage of high boiling compounds, had to be heated to a higher temperature (35° C.) in order to effect 100 percent decantation. At this temperature only 10 percent of the untreated sample could be decanted.

EXAMPLE II

A plant scale test was made to determine the effectiveness of the present invention under commercial operating conditions. Two clean 10,000 gallon tank cars were charged with commercial creosote from the same storage tank and at the same temperature (75° C.). To one car an aqueous solution, comprising 5 lbs. of "Polyox Coagulant" in 50 gallons of water, was added to provide a final condensate concentration of 0.005 percent by weight. Air agitation was employed during charging and mixing. The contents of the cars were allowed to cool and were thereafter examined and reheated with steam. The observations made during the test are shown below in Table II.

Table II

Creosote	Temperature, ° C.	Heating Time, Hours	Crystalline Residue in Car, Inches
Treated	6		18
Untreated	6		16
Treated	60	5	none
Untreated	60	6	8
Treated			
Untreated	71	7	6
Treated			
Untreated	77	8-10	4-6

The cars were then allowed to cool and were sent by rail to another plant. The following observations were made during the heating and unloading operations, which

occurred approximately two months after the initial charging:

Table III

Creosote	Temperature, ° C.	Heating Time, Hours	Crystalline Residue in Car, Inches	Remarks
Treated	−7		16	Crystalline Throughout.
Untreated	−4		16	
Treated	29	3.75	4–6	Do.
Untreated	29	3	27	
Treated	44	5	4	Air Agitation begun.
Untreated	46	5.5	16	
Treated	61	7.75	none	Pumped to storage.
Untreated	61	8.5	12–16	Agitation continued.
Treated				
Untreated	68	9.5	3–12	Began unloading.
Treated				
Untreated	77	10	3–4	

The data of Tables II and III clearly show the improved flow properties of creosote treated according to the method of the invention. The novel creosote composition of the invention was successfully rendered dischargeable after a 5-hour heating time at a maximum temperature of 60–61° C. In contrast therewith, a crystalline residue from untreated creosote remained in the car after a 10-hour heating period at a maximum temperature of 77° C.

EXAMPLE III

A series of tests were made as described in Example I to determine the effectiveness of various condensates in improving the flow properties of a commercial creosote containing 15 percent creosote crystals. The results are shown below in Table IV.

Table IV

Condensate	Control	"Tetronic [1] 908"		"Polyol [2] C-18604-G"		"Polyox Coagulant"
Estimated Molecular Weight of Condensate		27,000		20,000–40,000		1–10 million
Viscosity of a 1 percent by weight solution of condensate in water, centipoises		0.8		0.8		14,000–16,000
Concentration of condensate, percent by weight		0.0065	0.8	0.0065	5.5	0.005
Percent Water in Creosote	0.7	1.2	0.7	1.2	0.7	1.2
Results, percent by volume, decanted at:						
28° C.	0	0	0	0	0	5
33° C.	0	0	0	0	0	100
45° C.	5	0	5	0	5	
47° C.	70	5	100	0	5	
50° C.	100	60		20	100	

[1] A solid condensate of ethylene diamine with ethylene oxide and propylene oxide having a melting point of 58° C.

[2] A liquid condensate containing condensed propylene oxide.

It is seen from the data that only the high molecular weight (as determined by the viscosity test) polyoxyalkylene condensates are effective for purposes of the invention.

We claim:

1. Creosote containing a polyoxyalkylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water, in an amount of at least about 0.001 percent by weight and less than that which causes gelation of the creosote.

2. Creosote containing about 0.001–0.1 percent by weight of a polyoxyalkylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water.

3. Creosote having a lower flow temperature comprising creosote intimately admixed with about 0.001–0.1 percent by weight of a water-soluble polyoxyethylene condenate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water.

4. Creosote having a lower flow temperature comprising creosote intimately admixed with about 0.003–0.01 percent by weight of a water-soluble polyoxyethylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water and a melting point of 65–67° C.

5. Method of lowering the flow temperature of creosote comprising intimately admixing with creosote an aqueous solution containing between about 0.03 and 3 percent by weight of a polyoxyethylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water, in an amount of at least about 0.001 percent by weight and less than that which causes gelation of said creosote.

6. Method of rendering creosote readily dischargeable from containers comprising intimately admixing with creosote about 0.001–0.1 percent by weight of a polyoxyethylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water, as an aqueous solution containing between 0.03 and 3.0 percent by weight of said condensate.

7. Method of rendering creosote readily dischargeable from containers comprising intimately admixing with creosote 0.003–0.01 percent by weight of a polyoxyethylene condensate, said condensate being characterized by a viscosity of about 5,000–20,000 centipoises at 25° C. of a one percent by weight solution of said condensate in water and a melting point of about 65–67° C., as an aqueous solution containing between 0.03 and 3.0 percent by weight of said condensate.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 20, for "polyoxyethylene" read -- polyoxyalkylene --.

Signed and sealed this 5th day of December 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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USCOMM-DC