NEW APPROACHES TO CREATION OF LOW-TEMPERATURE COMPOSITIONS FOR PREVENTION OF COAL CONGEALING

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Kuzbass increases production and transportation of black coal. During the winter period there is congealing of coal mass and its freezing to the walls and the bottom of rail cars and dump trucks. Preventive liquids forming the low-freezing membranes used to be the main means of control.

New ideas of hydrogen bond (A.A. Grishayev) in water responsible for converging of water into ice and congealing of loads which are based on dynamic balance of long and short H-bond, allow to consider ice, water, and water solutions as dynamic systems with lifetime of 10^{-5}-10^{-12} seconds. In such systems the power centers of crystallization and structural waves due to long H-bonds, heteroatoms and other active particles are created. Blocking or destruction of such centers interrupts formation of ice or makes it inhomogeneous and fragile. This is affected by the introduction of alkyl, alkoxy, or acetyl radicals, Cl-anion, and the use of mixes of chemical compounds.

The example of a technical mix which forms a basis for creation of a preventive for the coal, walls and the bottom of rail cars is caprolactam production waste - the alkaline concentrate of caprolactam production (ACCP) on STO 05761637-003-2012 with a freezing temperature minus 37°C. Surfactants allow to regulate wetting, spreading and other indicators of a reagent.

Keywords: congealing of coal, striking toughness, strength of ice, SAW surfactants, reagents, freight, hydrophobic membranes, polymers of water.

Kuzbass is ramping up production and transportation of coal. Winter is the period of coal mass congealing; its adfreezing to the walls and bottom of the cars and trucks. The main means of combating these phenomena is to use preventive liquids, which form low-freezing membranes.

We have reviewed the proposals of the leading foreign companies Nalco, American Chemical Services Co and the American Chemical Services Associates, as well as Rosneftehim, Bashneftehimsnab and local producers supplying reagents for coal treatment against congealing. Today they use blue oils based on naphta (niogrin, severin, etc.), a mixture of alcohols (bottoms liquid, ketgol), aqueous solutions of glycols (ethylene and propylene) and salts (chlorides, acetates), solutions of solid paraffins in hydrocarbons, and al.

Most of the hydrocarbons compositions, alcohols, and aqueous solutions of glycols create antifreeze with a pour point of minus (40 - 60) °C. Some aqueous solutions have moderate freezing temperatures minus (5 - 30) °C, but they form a fragile structure of ice, which is easily destroyed during unloading. Paraffins form hydrophobic membranes on the surface of the coal and car walls.

New ideas of the hydrogen bonds (A.A. Grishaev) in water, responsible for the transformation of water into ice and congealing loads, which are based on the dynamic equilibrium of the long and short H-bonds,

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allow us to consider ice, water, and aqueous solutions as dynamic systems with lifetime of 10-5 – 10-12 seconds. These systems provide power centers of crystallization and structural waves due to long H-bonds, heteroatoms and other active particles. Blocking or destruction of such centers interrupts the formation of ice, or makes it uneven and fragile. The agents would be alkyl, alkoxy or acetyl radicals, anion Cl-, and mixtures of chemical compounds.

The advantages of preventive agents include not only the prevention of coal congealing and its adfreezing to the walls of the cars, but also reduced strength of the formed ice.

Ice and snow used to be polymers of water; they are in complex interaction with liquid water and monomer - H2O vapor. Ice has a heterogeneous structure, it includes several types of crystals, bubbles of gas (usually air), solids (minerals, organic compounds), and surfactants adsorbed on the boundaries of the phases. The pattern of this ice may serve frozen air foam of low expansion or foam plastic based on oligomers. Foam freezing slows down the processes of foam inner destruction, in foam plastic this process is not practically going on. The frozen foam is characterized by the intense sublimation of ice from the warmer layers into the cold ones. Creating hydrophobic membranes (partition) to the movement of water vapor inhibits this process. In some cases even monolayer membranes are effective: lauryl alcohol or polietilgidrosiloksan (NGL-94). Additives NGL-94 (up to 0.1 %) decrease the rate of ice sublimation 4 fold. Mixtures of surfactants are even more effective. Volgonat (0.1 %) and NGL-94 (0.006 %) reduce the flow of water vapor in 8.7 times [3].

The adsorption of surfactants saturation of the reaction mixture of plastic foams results in the mechanically fragile membranes and foam plastics. A similar phenomenon is observed in solidification of foam concrete at the excess of the surfactants in the solidifying suspension.

We have studied the effect of anionic surfactants of caprolactam alkaline concentrate (CAC) and added to it nonionic surfactant - PolyPnB on the ice strength. Along with the main components - sodium adipate CAC contains sodium salts of carboxylic acids, which are the typical anionic surfactants [1] and [2].

One of the mechanical strength characteristics under dynamic loads is resilience, which is identified by pendulum type device (Fig. 1 and Fig. 2) [4] and [5].

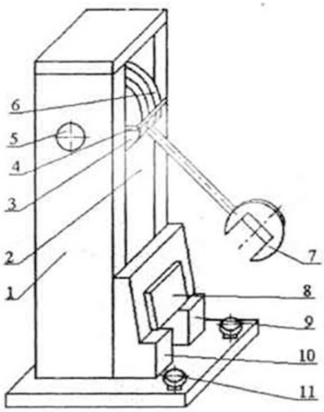

Fig.1. A device for determining resilience

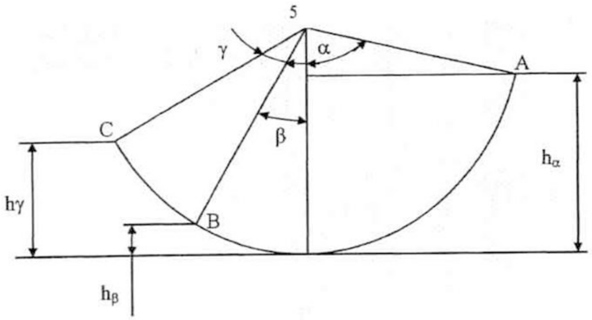

Fig. 2. A diagram of the pendulum impact.

Specific resilience a is equal to the energy U, spent on the destruction of the sample and divided by the cross-sectional area of the sample $A = h \times B$.

$$a = \frac{U}{A}, N \cdot m/m^2, \quad (1)$$

$$U = mgl\left[\cos\beta - \cos\alpha - (\cos\gamma - \cos\alpha)\frac{\alpha+\beta}{\alpha+\gamma}\right], \quad (2)$$

where:

m - mass, kg;
g - acceleration of free fall;
l - pendulum equivalent length;
α - pendulum angle of ascent;
β - the angle of the pendulum take-off after the sample destruction of (Fig. 2)
γ – the angle of pendulum in idling;
The scale unit is graduated in dimension U.

For the ice production we used: distilled water and 10 % solution of CAC with additives. Ice samples were prepared in metal molds of 100 × 26 × 23 mm, which, after filling the liquid were kept in a freezer at -21 °C for 4 - 24 hours. The test results are shown in Table 1.

Table 1 - The strength of ice

Samples of ice on the basis of	Cross-section h×B, mm	U, Nm	a, Nm/m^2
Distilled water	26,0×15,0	0,433	1110
Distil. water + 10% CAC	26,0×16,0	0,360	865
Distil. water + 10% CAC, soda 1% surfactant	26,0×15,0	0,263	653
Distil. water + 10% CAC, soda 0,5% surfactant and 0,5% oil	26,5×17,0	0,275	610

Anionic surfactants - CAC at a concentration of 10 % by weight reduces the strength of ice by 22.4 %. The presence of nonionic surfactant – PolyPnB, the content of which in the solution does not exceed 0.1%, the strength decreases even more – by 41.2 %. If the mixture of PolyPnB and oil is used as an additive to CAC, the result is improved by 45.09 %.

During this experiment, we studied coal congealing and adfreezing it to the metal walls under the laboratory conditions.

Experimental conditions: the temperature was minus 21°C. The coal of 0-3 mm with humidity of 3.4 % kept for a long time in the open air was not subject of congealing when loaded into a refrigerator compartment. The coal was humidified to 15 %, thoroughly mixed and kept in a sealed flask for 24 hours.

A portion of wet coal was placed in a flask with a stopper, an additive was put in an amount of 0.4 % of wt., and the content was thoroughly mixed. Then the samples were placed into a metal container and put in a freezer for 8-12 hours. The test results are given in the Table 2.

Table 2 - Coal congealing by humidity of 15% by weight.

№	Reagent	Observations
1	control (untreated)	Coal congealed, did not spill out of the container
2	Nalco	Coal spilled out, small agglomerates of coal observed
3	Polyglycols (DPG)	Coal spilled out of the container after three times shaking
4	Polyglycols + surfactants	Coal spilled out of the container after three times shaking
5	Polyglycol aqueous solution (VRPG)	Coal congealed, but in 0.5 of an hour spilled out without shaking

Samples 1,2,4,5 were kept in the open air for 24 hours at a temperature of minus 31-35 °C. The control sample 1 congealed, did not spill out. The results of treatment by reagents Nalco, polyglycols and VRPG were similar. Coal spilled out of metal containers, but we observed fragile agglomerates and light adfreezing to walls.

The second series of experiments was devoted to the study of brown coal with humidity of 30%. Coal is ground into powder for analysis. Adfreezing of treated or untreated by reagents brown coal to the walls and bottom of the container and congealing of the coal mass occurs at a temperature of minus 20 °C, provided its compaction. Without compaction the coal also congeals in mass but less adfreezes to the bottom and walls, if they are lubricated with the reagent. The observation results are shown in Table 3.

Table 3 - Coal congealing of 30 % wt. humidity

№	Reagent	Observations
1	control (untreated)	Coal froze on the walls and the bottom, did not spill out after 5 strokes
2	CAC ρ 1,210	Coal froze on the walls and the bottom, spilled out after 5 strokes
3	CAC ρ 1,210 + 1 % surfactant	Coal froze on the walls and the bottom, spilled out after 5 strokes, the surface is smoother
4	RPS-2, grade A	Coal froze on the walls and the bottom, spilled out after 5 strokes
5	RPS-2, grade B	Coal froze on the walls and the bottom, spilled out after 4 strokes

The study of coal congealing at minus 40 °C (climate chamber)

We used a metal model of a train car in scale 1:40. Load was 1.5 kg of steam coal, humidity 10.5 % by weight. There were three types of treatment: the surface of the car, the car surface + coal in bulk. Exposure in a chamber at -40 °C continued for 24 hours. The test results are shown in Table 4. The table shows characteristics of the reagents in accordance with the test procedure.

- Reagent CAC (production - "Azot", Kemerovo)

Reagent is a turbid viscous dark brown liquid with solids in the form of off-white flakes. It is easily sprayed, forms a stable membrane on the surface of the car. The reagent has an unpleasant characteristic smell. It preserves a limited fluidity at - 40 °C. The reagent showed the worse effectiveness then the control in all methods of treatment (-5 % to -21.4 %).

Coal from the train cars was unloaded in lumps from tight-loose to dense consistency. In the combined method of treatment the coal in train cars congealed into a monolith and could not be unloaded even while the car was under the conditions of room temperature for 15-20 minutes.

Table 4- Test results

Reagent	Type of treatment	The amount of the remaining coal in the train car				
		Without stroke	After the 1 stroke	After the 2 stroke	After the 3 stroke	After the 6 stroke
CAC	The control car (no treatment)	99,7	91,7	82,5	74,9	51,4
	Treated surface of the car	99,8	92,1	83,6	78,2	56,4
	Treated bulk of coal	99,9	91,9	85,1	82,4	65,5
	Treated surfaces and the bulk	100	96,8	93,8	90,0	77,8

	of coal					
RPS-2 Grade B	The control car (no treatment)	99,6	80,4	63,2	27,1	12,1
	Treated surface of the car	99,6	81,3	68,3	60,7	0,0
	Treated bulk of coal	99,7	83,2	58,3	26,6	0,0
	Treated surfaces and the bulk of coal	99,8	86,1	74,5	64,4	15,0
RPS-2 Grade A	The control car (no treatment)	100	88,3	79,2	64,2	24,4
	Treated surface of the car	100	91,9	86,4	68,0	31,4
	Treated bulk of coal	99,8	89,8	81,2	76,4	20,5
	Treated surfaces and the bulk of coal	99,9	84,3	74,2	55,5	4,8

- Reagent RPS-2 grade B (experimental sample, KemTIPP, Kemerovo)

The reagent is turbid dark brown liquid with a specific smell. It is well sprayed, forms a membrane, some quantity of the reagent is dripping from the walls of cars on the bottom. It is fluid at -40 °C.

The reagent showed better effectiveness then the control in treating coal in the bulk and on the car surface (in both cases + 12.1 %). In the combined method of treatment the effectiveness was a little worse than the control (-2.9 %).

The coal is unloaded from the car in lumps of tight-loose consistency.

- Reagent RPS-2 grade (experimental sample KemTIPP, Kemerovo)

The reagent is a clear, dark brown liquid with a characteristic smell. Sprayed well, but during the surface treatment the reagent flows down to the bottom of the car due to the low viscosity. At -40 ^{O}C it remains fluid. In the treatment of surfaces of cars the effectiveness was worse than the control (-7.0%). During treatment of coal in bulk and combined treatment method the reagent showed better efficiency then control (+ 3.9 % and + 19.6 % respectively).

The coal unloaded from the cars was in the form of loose lumps.

The development of improved reagent based on CAC.

The results of laboratory and production tests suggest RPS-2 grade A and grade B as the reagents against congealing. The indicators of these reagents are presented in Table 5.

Table 5 - Indicators of RPS-2 grade A and B

Indicator	Standard		Method of treatment
	Grade A	Grade B	
1.Visual look	Liquid from brown to dark brown color, opaque, with no visible mechanical impurities	Liquid from light yellow to brown color without mechanical impurities	In para. 4.3 of current specifications
2. Density at 20 ° C, g / cm^3 in the range	1,152 - 1,185	1,070 - 1,120	According to GOST 18995.1 Section 1
3. Congealing temperature, °C in the range	minus 30 - minus 35	minus 40 - minus 45	According to GOST 20287 p. 2 and Method B and p. 4.4 of current specifications
4. Hydrogen ions activity, pH units, in the range	8 - 10	8 - 10	According to GOST R 50550 and paragraph 4.5 of current specifications

Grade A provides the operating temperature of the reagent to minus 30 - 35 °C by applying a dilute solution of CAC with 1,152 - 1,185 density. The temperature range of minus 40 - 45 °C is achieved by adding a water-glycol mixture of HCV to CAC. Grades A and B have lower indicators of viscosity, and surface tension than CAC, which provides good dispersion through the nozzles under experimental and industrial conditions.

The reagent has been subject of patent application number 201403821.

Conclusion.

1. A reagent against congealing RPS-2 has been developed, which comprises a combination of the following factors.

RPS-2 Grade A has a density of 1,152-1,185 and pour point temperature of minus 30-35 °C.

RPS-2 Grade B has a density of 1,070-1,120 and pour point temperature of minus 40-45 °C.

2. Reagent RPS-2 has been tested in the laboratory and partially in an industrial environment (Borodinsky open cast - CAC + 0.08 surfactants), showed good dispersion via nozzles.

3. Reagent RPS-2 has advantages over CAC on the reagent consumption per m^2 of the surface and on the reduction of the ice strength (if any).

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