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Environmental benefits of new industrial waste-based lubricant compositions

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Abstract. Innovative industrial waste-based lubricants are analyzed. The lubricants based on spent diesel oil, low molecular weight polyethylene, polysulfide polymers and petroleum coke can reduce the cost of lubricants without reducing their technological characteristics. Polysulfide polymers synthesis from trichloropropane is described. Efficiency of the proposed lubricant is higher in comparison with pure spent diesel oil or spent diesel oil with addition of graphite.

1. Introduction

At present, strict environmental requirements are imposed on lubricants [1]. Lubricants are used to prevent rails and wheel pair flanges from lateral wearing when passing curved track sections. They reduce energy costs but pollute the environment and worsen the ecological situation near the railways. Therefore, along with technological and economic requirements, such lubricants have to meet the following environmental requirements:

1. Lubricants should not contain components which are toxic to humans and animals.
2. Lubricants should not contain volatile substances which pollute the atmosphere.
3. Lubricant components should gradually decompose in the environment forming harmless compounds.
4. Lubricants should not contain substances which are easily washed away by precipitation, get into water objects adjacent to the railway and worsen the ecological situation.

Unfortunately, some rail lubricants contain A-76 gasoline. Evaporating gasoline leaves a polymer film on the lubricated surface which serves as a lubricant. Among these lubricants are PC-6, PC-6 "V", PC-6 "Vu", RAS-1, etc. A large number of volatile hydrocarbons thrown into the air pollute the environment.

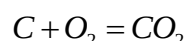
A lot of foreign lubricants contain surface-active substances (lithium, calcium, aluminum salts of higher carboxylic acids – soaps) which are easily washed out from the applied lubricant with atmospheric precipitation and fall into nearby water objects. In addition to environmental degradation, these substances provoke corrosion processes in metal structures near the wheel-rail friction unit and increase the amount of heavy metals in the environment.

Some Russian rail lubricants (widely used by the Russian Railways) contain molybdenum disulfide which is an excellent antifriction material decreasing the coefficient of friction. This substance is water-insoluble. However, in the external environment, it turns into compounds containing soluble



forms of molybdenum. Molybdenum compounds affect warm-blooded animals and humans. Their effects on lower organisms have not been studied yet. Therefore, the use of molybdenum disulfide lubricants can cause irreversible environmental damage.

Since July 1997, instead of RS-6 "V" and RP-1, pure spent diesel oil or diesel oil with addition of graphite has been widely used by the East-Siberian Railways company [2]. The lubricant reduced rail wear between Irkutsk and Andrianovskaya stations three-five-fold. The lubricant has a minimal environmental impact, since it does not contain volatile and toxic compounds. Hydrocarbons in the composition of spent diesel oil are environmentally "soft" compounds. Exposed to light, oxygen and microorganisms, they decompose easily and form harmless substances, mainly carbon dioxide and water. Finely divided graphite is gradually oxidized to carbon dioxide:



However, it is difficult to keep these lubricants (especially pure ones) on the side rail surface. The lubricants contain an expensive graphite component. According to Novomoskovsk chemical plant, the cost of finely divided graphite production is about \$20 000 per ton.

Lubricants based on spent diesel oil, low molecular weight polyethylene, polysulfide polymers and petroleum coke can reduce production cost without reducing technological characteristics [3, 4]

Low molecular weight polyethylene is a polyethylene production waste product. It consists of normal hydrocarbons with an average molecular weight of 1500 units. These hydrocarbons are non-toxic. Externally influenced, they decompose easily [5].

The chemical composition of petroleum coke is similar to that of graphite, i.e. it consists of carbon. However, having a more porous structure consisting of small crystallites, it oxidizes much more easily in the environment exposed to light and oxygen.

2. Materials and methods

For research purposes, spent diesel oil, low molecular weight polyethylene, polysulfide polymers and petroleum coke were used. Polycondensation methods were used for synthesis.

3. Results and analysis

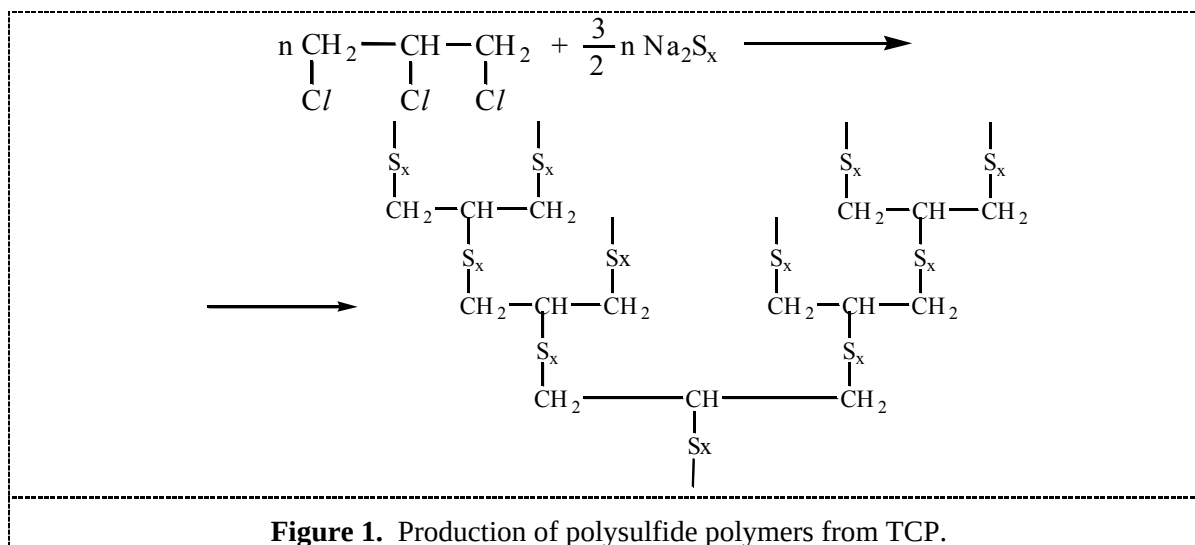
Sulfur-containing polymer is introduced into the composition in an amount of 5-10% of the total weight of the composition. Sulfur in these polymers is transformed into surface iron sulfides which give a protective effect to the lubricant. The undecomposed part of the polymer is exposed to microorganisms. Lubricants with addition of other components decompose faster than pure polymers [6].

Polysulfide polymers from trichloropropane.

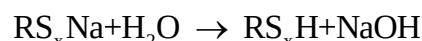
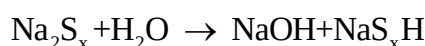
When using trifunctional monomers, crosslinked polymers are formed. This is also true for polysulfide polymers derived from 1,2,3-trichloropropane (TCP) [7]. These polymers had poor technological properties, so they did not find industrial application. Only partial reductive splitting by disulfide bonds is described. It decreases molecular weight and improves performance [8, 9]. Disinterest in these polymers might be due to the fact that they are used only as sealants.

Considering the possibility of using polysulfide polymers as components of lubricant compositions where solid easily powdered polymers are required, we carried out polycondensation of TCP in the aqueous hydrazine-alkali system using sodium polysulfide. During previous experiments, polymers were produced by the same method using the following ratio of NaOH: S = 1: 1.3 ($Na_2S_{2.6}$) in order to synthesize tritoglycerol [10]. Polymers were produced with a yield of 95%, however, no physical and chemical characteristics were described.

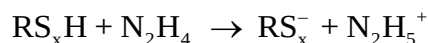
We studied the possibility for producing polysulfide polymers from TCP in the aqueous hydrazine-alkali system. In the system, Na_2S_x was generated with various degrees of polysulfide by varying the S: NaOH ratio. Production of these polymers called dendrimers [cf. 10] is presented in Figure 1.



The content of residual chlorine increases with a decrease in the amount of polysulfide (x in Na_2S_x) and decreases with an increase in the amount of hydrazine. The latter fact may be due to participation of hydrazine as a base for hydrolysis of sodium polysulfides and sodium thiolates in the aqueous solution:



Hydrazine (a sufficiently strong base) shifts hydrolysis equilibrium to the left. More over, it can enter into acid-base reactions:



As far as anions S_x^{2-} and R^-S_x^- are more reactive than HS_x^- and RS_xH in nucleophilic substitution reactions, chloride has a higher substitution degree in experiment 6 than in experiment 5.

An increase in the content of residual chlorine with a decrease in the content of polysulfide in the solution can be determined by lower availability of carbon atoms to the nucleophilic attack in more closely spaced propane fragments (the length of the $\text{C}-\text{S}-\text{S}$ bonds is shorter than the length of the $\text{C}-\text{S}-\text{S}-\text{C}$ and $\text{C}-\text{S}-\text{S}-\text{C}$, etc.).

Heated polymers with $x \geq 2$ become viscoplastic. When cooling these melts, dark colored polymers have rubber-like properties.

4. Discussion

Transition of heated polymers into a viscoplastic state may be caused by breaking of the $\text{S}-\text{S}$ bonds in their molecules under heating. That thermal splitting of $\text{S}-\text{S}$ bonds can form intramolecular cyclic fragments reducing the branching of the polymer which becomes rubbery when cooled.

The polymer produced from sodium sulfide ($x = 1$) does not become liquid. Its darkening is observed only at temperatures above 260°C . At temperatures above 330°C , it decomposes and does not form liquid or coking products in the capillary or on the plate.

In the IR spectra of the polymers, there are bands characterizing the $\text{C}-\text{H}$, $\text{C}-\text{S}$ bonds, and for polymers with $x > 2$, there are $\text{S}-\text{S}$ bonds (460 cm^{-1}).

5. Conclusion

Thus, in the aqueous hydrazine-alkali system, solid powdered polymers were produced from TCP. In the powdered state, they can be introduced into lubricating compositions. However, TCP is an

expensive monomer. The main industrial TCP production method is allyl chloride isolation from production waste. Allyl chloride is used for epichlorohydrin production [11, 12, 13, 14]. Cheaper components should be used for introducing into rail lubricant compositions.

Opportunities for producing polysulfide polymers using production waste were described.

Efficiency of the proposed lubricant is higher in comparison with lubricants based on pure spent diesel oil or spent diesel oil with addition of graphite.

In terms of environmental protection, it is necessary to consider them as a whole, taking into account the fact that they consist of chemical and petrochemical waste. They had a greater impact on the environment than any lubricant compositions used for rail lubrication.

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