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Production of Sulfur-Containing Polymers on the Basis of Petroleum Refining and Chloroorganic Wastes

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The possibility of the simultaneous treatment of petroleum refining and chloroorganic wastes (COW) has been shown. COW are complex mixtures of organic polychlorides. At present there are no effective and ecologically safe methods of COW remaking in the industrial practice. In fact, COW combustion or burial are used. Both are ecologically dangerous and can be used only as temporary measures.

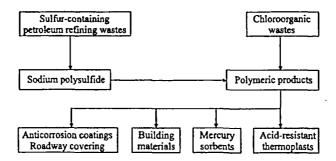
The proposed treatment is based on the polycondensation of a mixture of organic polychlorides with sodium polysulfide. The latter can be produced from petroleum refining wastes (gas sulfur, H₂S, alkaline solutions discharged after H₂S absorption, etc.). Variation of the reaction conditions allows binding of any chloroorganic compounds to polymer structures. As a result the COW toxicity is eliminated. The principal factor determining the choice of reaction conditions is the COW composition, namely, the content of chlorobenzenes and chloroethylenes. It is known that the nucleophilic substitution of chlorine atoms in alkane derivates proceeds readily. At the same time chlorobenzenes and chloroethylenes are poorly active in these reactions.

For these reasons the treatment of COW containing mainly chloroalkanes (vat residues of vinyl chloride production, for example) does not encounter particular difficulties. The reaction of these wastes with aqueous sodium polysulfides at a temperature below 100 °C leads to the formation of rubber-like products. The treatment of COW containing considerable amounts of benzene and ethylene chlorides (the heavy fraction of epichlorohydrin production wastes, which contains up to 50 % of hexachlorobenzene, for example) presents a more serious problem. The chlorine nucleophilic substitution in the aromatic compounds can be carried out in dipolar aprotic solvents (DAS). However these reactions need high temperatures.

The use of phase transfer catalysts (PTC) allows the reaction to be carried out under mild condition (60-95 °C) without DAS. Tetraalkyl ammonium derivates or water-soluble polycations with quaternary nitrogen atoms in the macromolecular units, such as polydimethyl diallyl ammonium chloride, for example, can serve as PTC. The catalyst expenditure is 0.5-3.0 % of the COW mass. The sodium polysul-fide/COW ratio is a very important factor of the proposed process, which should be not less than 10 mol/kg. Otherwise the polymer yield and degree of chlorine substitution decrease in several times. The polymers obtained by sulfidizing of the wastes of epichlorohydrin production contain up to 85 % of sulfur. They are thermoplastic even at high degrees of chlorine substitution (the initial and residual chlorine content is 80 nd 5 %, respectively). This is explained by the cyclic-chain structure of these polymers.

The polymers obtained can be compatible with polyvinyl chloride, epoxide compounds, and solid bitumens. As a result, this leads to an increase in acid-resistance of the polymer compositions and the heat distortion temperature of solid bitumens and to a decrease in expenditure of the epoxy resin hardeners. These polymers eliminate mercury and its compounds from water and gases. The sorptive capacity of these polymers achieves 180 mg Hg per 1 g.

The scheme below demonstrates the possibility of the treatment of the petroleum refining and the chloroorganic wastes.



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