UDC 661.723 + 547.362.365

Novel Approaches to the Utilization of Large-Tonnage Industrial Wastes Such as Hydrolytic Lignin, Sulphur, Polychloroaliphatic Compounds

A. F. GOGOTOV^{1,2}, V. R. STANKEVICH¹, V. P. KISELEV³, A. A CHAIKA² and V. G. DRONOV²

¹Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, UI. Favorskogo 1, Irkutsk 664033 (Russia)

E-mail: alfgoga@mail.ru

²Irkutsk State Technical University, Ul. Lermontova 83, Irkutsk 664074 (Russia)

³Siberian Federal University, Pr. Svobodny 79, Krasnoyarsk 664041 (Russia)

(Received December 18, 2012)

Abstract

Organochlorine wastes generated in the production of epichlorohydrin, and lignin could be co-processed to obtain the sulphur-containing derivatives. For this purpose, the wastes of chloroorganic synthesis and hydrolytic lignin chlorinated under mild conditions should be entered into the reaction with sulphur in the form of sodium polysulphides. The overall process is cost-efficient due to the fact that it provides an almost complete conversion of organochlorine waste disposal, sulphur compounds as well as lignin binding. The condensation products obtained were tested as additives for modifying bitumen and demonstrated a good processability.

Key words: lignin, organochlorine residues, sodium polysulphide, condensation products

INTRODUCTION

Currently the consumption of organic resources has become global, but it is not a complex case and being accompanied by the formation of a great amount of non-utilizable wastes, which leads to the accumulation thereof to cause environmental problems. In this regard, the development of waste utilization technologies for the main industries remains a topical problem.

At present time, in Russia at all the hydrolysis plants there has been a significant amount (about 95 million ton) of non-recycled hydrolytic lignin (HL) accumulated [1]. Since the hydrolytic lignin represents a substance with a low reactivity [2], it should be preliminary activated. The most common method for activating the HL consists in alkaline cooking thereof at 170 °C in a 1 M NaOH solution [3]. A variant of neutralizing the side organochlorine products of synthesis *via* condensing them with HL [4, 5] after the activation of lignin by alkali with the concentration of 40-50 %. This technique of HL activation low-tech, so it is required for using other, simpler and more efficient methods for the activation.

In recent years, there is increasing the demands observed concerning the quality of fuel, in particular, sulphur content therein [6]. Consequently, in the petrochemical complex there increases dramatically the production of sulphur in the Claus process. The problem of sulphur utilization becomes more and more urgent every year, however, there has not been any acceptable solution found yet, which could potentially create serious environmental problems. A variant of utilizing the sulphur in the form of sulphur concrete for road construction proposed within the last decade having all the positive properties exhibits a number of disadvantages. For example, this approach does not solve the problem of the microbiological stability of sulphur concrete and of the flammability of such road asphalt compositions obtained. For this purpose, the sulphur should be bound more reliably into a condensed sulphur-containing composition.

A severe environmental hazard is resulted from the production of organochlorine compounds belonging to the aliphatic series, in particular epichlorohydrin. In the course of obtaining the epichlorohydrin *via* high-temperature chlorination of propylene, besides the main product of chlorination – allyl chloride – there appear a great amount of side chloro-containing organic substances (COS), such as monochloropropene, dichloropropenes, dichloropropenes, trichloropropanes *etc.* [7].

Nowadays, there are no environmentally safe and economically acceptable industrial technologies either for processing these wastes into practically valuable products, or for disposing thereof.

The aim of this work consisted in developing a comprehensive method for the disposal of large-tonnage wastes from three industrial branches such as hydrolytic, organochlorine synthesis and refining industries.

EXPERIMENTAL

Activation of hydrolytic lignin

We used HL taken from the Krasnoyarsk Biochemical Plant (Krasnoyarsk, Russia) with the humidity level ranging within 46–52 % and the ash content amounting to 6.2 %, containing 68.1 % of carbon, 6.4 % of hydrogen, and 12.3 % of extractive substances. The hydrolytic lignin was sieved through a sieve in order to remove coarse fractions and inclusions greater than 2 mm in size in an amount of 100 g (calculated for the anhydrous product) were placed in a flask, wherein there was previously poured 1 dm³ of chlorine water with the active chlorine content of 7.0–14.0 g/dm³ (at the temperature of the solution equal to 12–15 °C) [8]. The suspension was held

for 1–2 h, with a periodical stirring. After this time, the aqueous phase was examined for active chlorine content and, in the case of the absence of the chlorine; the chlorolignin was filtered and washed with water up to obtaining a neutral pH value of the washing water. The modified lignin obtained was dried up to a moisture content of 40-60 %. For the samples obtained, the content of chlorine as determined. The chlorine content in different samples of chlorinated lignin ranged from 3.5 to 28.8 %.

Condensation reaction between COS and activated hydrolytic lignin

The resulting product *i. e.* hydrolytic lignin activated by chlorination with a known content of chlorine (composition (%): Cl 14.2, C 57.9, H 6.6) in an amount of 50 g (calculated for anhydrous product) was placed in a threenecked round-bottom flask equipped with a stirrer, reflux condenser and a dropping funnel. Was added 200 cm³ of water, 41.86 g of $Na_2S \cdot 9H_2O$ (13.6 g, calculated for anhydrous Na_2S), 5.6 g of sulphur and 7.2 g of NaOH. The mixture was vigorously stirred, heated on a steam bath up to 60-95 °C to hold with constant stirring for 1 h. Further, a weighed sample portion of COS (in this case a mixture of 1,2- and 1,3-dichloropropanes, 1,3-dichloropropene and 1,2,3-trichloropropane in an arbitrary ratio) with the mass of 13.2 g was put in a flask (at a rate of 1 cm³ every 15 min) at a temperature of 60-95 °C, to hold at this temperature for 3-4 h. Periodically (every 30 min), the acidity of the reaction medium $(pH \ge 8)$ was controlled. After completing the process, the pH value was checked and the reaction mixture was then acidified up to pH 2, then it was filtered, washed with water and dried. The filtrate was extracted with chloroform; the extract was analyzed for the content of unreacted COS with the use of GLC technique. A sample of the reaction product has the following composition (%): C 33.1, H 7.1, S 9.6, S 13.2. No source COS used for the condensation reaction was detected in the extract.

The physical and mechanical properties of asphalt concrete samples were determined using standard methods (State Standard GOST 12801–98).

RESULTS AND DISCUSSION

We propose a scheme of integrated waste utilization in different industries *via* co-processing thereof into a product that meets the requirements of the road construction industry [9].

The scheme proposed could be presented as it follows:

1) sulphur is used to produce sodium polysulphide according to the reaction

 $Na_2S + xS \rightarrow Na_2S_{x+1}$

2) lignin undergoes the activation to obtain chlorinated hydrolytic lignin (CHL) *via* mild chlorination according to the conditions described by the authors of [9]:



3) organochlorine wastes from the production of epichlorohydrin in the mixture with CHL are processed by sodium polysulphide (SPS) in an alkaline medium according to the general scheme (Scheme 1).

IR spectra of CHL exhibit absorption bands at 1612 and 1610 cm⁻¹ those characterize the carboncarbon bonds of the benzene ring; the absorption bands at 1465, 1461 and 1125 cm⁻¹ are related to the vibrations OCH₃ groups, as well as the absorption bands at 730 and 850 cm⁻¹ correspond to C–Cl bonds in the ring and the side chain.

The examples of CHL condensation with COS in the presence of SPS obtained *via* the reaction between sodium sulphide and sulphur are presented in Table 1. It is seen that the scheme proposed for the neutralization of organochlorine wastes *via* co-condensation of HL activated by chlorination and CCOS in the presence of the SPS in alkaline medium exhibits a high selectivity and efficiency as far as the binding of toxic chloroaliphatic compounds is concerned. Changing the mechanism of binding COS with activated HL leads to a considerable reduction in the consumption of alkali in the



benefite 1.

TABLE 1

Conditions of chlorinated hydrolytic lignin (CHL) condensation with COS in the presence of sodium polysulphide (SPS)

Chlorine content	COS	Mass, g	2			CHL and COS condensation (in the presence of SPS) product content, $\%$		
in CHL, $\%$		COS	Anhydrous	S	NaOH			
			Na_2S			S	Cl	
0*	1,2,3-TCP	13.2	-	_	72.0	-	0.4	
3.5	1,2-DCP	7.0	6.8	1.4	6.0	4.2	0.9	
7.3	1,3-DCPen	8.8	6.8	2.1	6.0	5.4	1.3	
10.2	1,3-DCP	10.2	10.2	2.8	6.6	6.8	2.2	
14.2	1,2,3-TCP	13.2	13.6	5.6	7.2	9.2	2.8	
14.2	Mixture	13.2	13.6	5.6	7.2	9.6	3.2	
20.9	«	26.4	20.4	8.4	7.5	25.8	4.1	
28.8	«	35.0	27.2	11.2	9.0	31.7	8.1	

*Hydrolytic lignin modified according to conditions reported in [4].

Sample Mixture composition Penetration Fragility Softening Resistance No. level at 25 °C, temperature, point, °C to aging, °C* 0.1 mmby Fraas, °C 1 Original bitumen BND90/130 128 -17.045.052.02 Original bitumen 121 -19.046.050.5 + modified HL [4] 3 Original bitumen 118 -20.147.551.5+ product of COS and CHL co-polycondensation 4 Original bitumen 104 -20.849.0 53.0+ product of COS and CHL co-polycondensation with SPS

TABLE 2

Physical and mechanical characteristics of the original bitumen and composite binder based on bitumen with COS, CHL and sodium polysulphide (SPS) co-polycondensation products. The ratio original bitumen/modifier = 95 : 5

Note. Samples Nos. 3 and 4 correspond to samples Nos. 5 and 7 in Table 1.

*Resistance to aging was assessed from changing the softening temperature after heating under the test conditions according to State Standard GOST 18180–72 (after heating at 163 $^{\circ}$ C for 5 h).

condensation process, as well as to complete abandoning the use of alkali at the stage of lignin activation.

All the mentioned absorption bands remain observed in the IR spectra of the products of the reaction between COS and CHL in the presence of SPS. This indicates that CHL is included as a part of the polymer products obtained. Thus, the COS are grafted to the side alkyl chains of lignin *via* sulphur-containing bridges $S_{x + 1}$, almost without affecting the phenolic hydroxyl groups of lignin to save thereby the properties thereof as an antioxidant.

The analysis of the data in Table 1 demonstrates that the products of CHL and COS condensation in the presence of SPS contain, alongside with sulphur, a certain amount of chlorine. According to IR spectroscopy, the chlorine under determination is bound to the aromatic ring of the lignin (C_{ar}-Cl bond indicated by conserving the absorption bands at 730 and 850 cm^{-1}). Furthermore, there is a C_{aliph} -Cl bond revealed in COS, which is indicated by the presence of the absorption band at 680 cm^{-1} . Therefore, under these experimental conditions the COS undergo condensation with the propane side chains of lignin to substitute chlorine therein. The presence of C_{aliph} -Cl bond in the condensation products indicates an incomplete substitution of CCOS chlorine by sulphur in the course of the condensation.

Grafting the COS on the side chains to a considerable extent causes the HL to turn into a derivative of alkylbenzenes with long alkyl chains, which leads to increasing the surfactant properties of the derivatives. The presence of sulphur in the side chain near the free phenolic hydroxyl enhances the antioxidant properties of the modified lignin. The presence of chlorine in the aromatic ring of the lignin enhances the biostability of sulphur-containing bituminous composition.

The resulting product of COS and CHL copolycondensation with SPS was tested as a modifier of a bituminous composition. The results of studying the physical and mechanical properties of the modified bitumen are presented in Table 2. One can see that, in contrast to the data concerning the bitumen modification by original HL, the preliminary reaction between lignin and COS and especially the product of CHL and COS condensation in the presence of polysulphides allow increasing the compatibility between bitumen and lignin from 6-7% to 20-22% in the case of COS condensation with modified lignin and sulphur. As a consequence, an increased compatibility results in improving of some qualitative characteristics of bitumen. Lowering the penetration level at 25 °C inherent in all the modified samples, leads to a more stable consistency of the asphalt concrete mixture.

For the modified samples, one can observe a higher softening temperature (determined according to the ring and ball technique). In the case of introducing such bitumen into the asphalt concrete composition, an increase in the heat resistance is observed. The proposed additives, as to compare with the original bitumen (sample No. 1) cause the temperature of the modified binder fragility to decrease by 11.76, 18.23 and 22.35% for the samples Nos. 2-4, respectively. Lowering the temperature of the binder fragility exerts a direct effect on the frost resistance of an asphalt concrete pavement, causes the resistance of the top layer of the pavement to increase with respect to the formation of transverse cracks in the wintertime of road management. As one can see from Table 2, all the modified samples of the organic binder, especially Nos. 3 and 4 are characterized by an increased resistance with respect to oxidative degradation under the conditions of testing in accordance with the State Standard GOST 18180-72. This exerts a positive effect on the resistance of an asphalt concrete pavement with respect to the formation of waves and a deep-rut character within the period of high positive temperature values in summer.

Basing on bitumen BND60/90 with the addition of chemically modified lignin in an amount ranging from 3.5 to 10 % with respect to the mass of bitumen, we prepared the samples of asphalt-concrete with the following composition (mass %): gravel with the fraction size 5-10 mm fraction -18 %, 10-20 mm - 17 %, sand -53 %, mineral powder -12 %, bitumen BND60/90 + modified lignin (7.8 mass %) -7 % (above 100 %).

The investigations have demonstrated that at the processing temperature of 160-170 °C for preparing the organomineral mixture the composite binder with the products of chlorolignin interaction with sulphur and COS are evenly distributed over the surface of gravel grains in accordance with the gravity and capillary surface forces in the material. The additives proposed to an insignificant affect the brittleness temperature of the composite binder to promote the reduction thereof. The brittleness temperature of the original bitumen was equal to -17.0 °C. For all the samples obtained, the brittleness temperature values determined by means of the Fraas method were equal to -19.0...-0.8 °C (in accordance with the State Standard GOST 222245-90 the normal value should be not less than -17 °C). All the types of the binder used withstand the cohesion with marble according to the control sample.

The penetration index corresponded to the requirements of the State Standard GOST 222245–90, ranging from -1.0 to +1.0; the extensibility of all the samples was equal to at least 70 cm.

The results of testing the asphalt concrete samples are presented in Table 3. It is seen that

TABLE 3

Sample No.	Density, g/cm ³	Swelling, vol. %	Bulk water saturation, vol. $\%$	Compressive strength, 10^5 Pa, at the temperature, °C		Water resistance coefficients under water saturation, days		
				20	50	1	14	30
0*	2.30	0.43	5.30	26.2	10.6	0.76	0.67	n/d
1	2.33	0.45	6.11	29.9	11.8	0.88	0.74	n/d
2	2.37	0.59	3.83	36.0	13.4	1.15	0.96	0.62
3	2.34	0.14	4.70	37.6	16.2	1.14	0.97	0.91
4	2.39	0.32	2.71	33.1	11.2	0.89	0.75	n/d
5	2.36	0.13	4.07	34.2	12.8	0.90	0.82	n/d

Physical and mechanical properties of organomineral mixtures obtained basing on the binders composed of bitumen and modified hydrolytic lignin

Notes. 1. Samples Nos. 1-5 – mixtures based on hydrolytic lignin modified by COS wastes a sulphur-containing petrochemical wastes: No. 1 – under the conditions of [4], No. 2 – chlorinated HL (10.2 % Cl), Nos. 3-5 – corresponding to samples Nos. 4-6 in Table 1. 2. n/d – no data.

*Mixture based on the original bitumen.

the use of modified HL in composite binders allows one to obtain organomineral mixtures with a higher compression strength at 20 and 50 °C and with an increased resistance with respect to water under short-time (1 day) water saturation. The tests performed demonstrate that the use of HL treated industrial wastes from organochlorine synthesis industry and of sulphur-containing wastes from petrochemical industry, as bitumen-modifying additives (in the amount of 7.8 % from the mass of the composite binder) allows 25–30 % increasing the water resistance level after water saturation for 30 days, and 20–38 % increasing the frost resistance level after 25 freezing-thawing cycles.

Basing on testing the proposed samples, we could conclude that all the investigated samples of asphalt concrete mixtures to a complete extent meet the requirements of the State Standard GOST 9128–97. Such mixtures could be used in the upper layers of pavements. This indicates the potentiality of using the obtained modifying additives in road construction industry.

These results demonstrate that the composite binder exhibits increasing the number of active functional groups and sulphur-containing free phenolic hydroxyl groups (owing to the introduction of phenolic hydroxyl groups contained in lignin). The proportion of functional groups imparting surfactant properties to the samples exhibits an increase, too. Such changes in the structure of the composite binder as to compare with pure bitumen provide a substantial activation of chemisorption processes to improve the main operational properties of asphalt concrete.

Taking into account an almost inexhaustible resource of HL, significant reserves of toxic COS at the enterprises of organochlorine synthesis and an excess of sulphur in oil refining industry, we could assume a variant of rational targeted using large-tonnage and related organic production waste for road construction to be found that consists in simple co-polycondensation thereof under relatively mild conditions. This allows one not only to convert the waste into a recyclable and consumable product of road construction, but also to significantly improve the environmental condition of enterprises and regions with developed multisectoral chemical industry.

In contrast to the solutions earlier known concerning the processing of HL the method

proposed for the substrate (technical HL) activation is quite manufacturable being performed under mild conditions via simple mixing the lignin with chlorine water [8]. The chlorinated lignin obtained reacts in the presence of aliphatic polychlorinated compounds with sulphur-containing reagent such as sodium polysulphide via occurring a simple alkaline condensation process, which provides power consumption in the course of obtaining thereof to decrease. The presence of alkali is necessary for binding of chlorine displaced, and, in addition, for decreasing the probability of decomposing the polysulphide that acts as a basic reagent involved in the substitution of chlorine both in the COS and in the chlorinated lignin.

CONCLUSION

Thus, a comprehensive method has been proposed for utilizing large-tonnage wastes resulting from three major industries (hydrolysis, organochlorine synthesis and petroleum processing) with obtaining a product promising for using in such a resource-demanding industry as road construction. The technical solution found [9] has been included in the register of "100 Best Inventions of Russia" for 2009.

REFERENCES

- Budaeva V. V., Mitrofanov R. Yu., Zolotukhin V. N., Obrezkova M. V., Skiba E. A., Ilyasov S. G., Sakovich G. V., Oparina L. A., Vysotskaya O. V., Kolyvanov N. A., Gusarova N. K., Trofimov B. A., *Polzunov. Vestn.*, 4, 1 (2010) 158.
- 2 Gogotov F. A., Luzhanskaya I. M., Chem. Sustain. Dev., 5, 3 (1997) 279.
- 3 Chudakov M. I., Promyshlennoye Ispolzovaniye Lignina, Lesn. Prom-st', Moscow, 1983.
- 4 RU Pat. No. 2079477, 1997.
- 5 Platonov A. Yu., Mayorova E. D., Evstigneev E. I., Sivakov A. A., Kruglov A. S., Kurzin A. V., 1 Soveshch. Obyed. Uch. Soveta po Org. Khim. UrO RAN "Lesokhimiya i Org. Sintez" (Thesises), Syktyvkar, 1994, p. 53.
- 6 Lapidus A. L., Golubeva I. A., Bolotina M. V., Neftepererab. Neftekhim., 9 (2006) 25.
- 7 Voronkov M. G., Korchevin M. A., Russavskaya N. V., Tomin V. P., Deryagina E. N., *Khim. Ust. Razv.*, 9, 6 (2001) 541.
- 8 Turetskiy Ya. M., Shorygina N. N., Izumrudova T. V., Gristan E. L., Gidroliz. Lesokhim. Prom-st', 8 (1961) 10.
- 9 RU Pat. No. 2376275, 2009.