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Products of the Reaction of *N*-Monochlorosufonamides with Isobutylene–Styrene Oligomers as Additives for Lubricating Oils

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Abstract—The reaction between *N*-monochlorosufonamides and a low-molecular-mass isobutylene–styrene cooligomer in the presence of inorganic acids was studied. It was found that regardless of the substituent (hydrogen or alkyl radical) on the sulfonamide nitrogen, the reactivity of *N*-monochlorosulfonamides is very high and results in the formation of *N*-β-chloropolyalkylarylsulfonamides in a reaction with a polymer. The high yield of the product of the *N*-chlorosulfonamide reaction with the polymers is reached within 3–4 h at 50°C. It was revealed that the addition of *N*-ethyl-*N*-chloroarylsulfonamide to unsaturated groups proceeds easier as compared to other *N*-monochloroamines, and the yield of the desired product reaches 90%. The products exhibit high anticorrosive and tribological behavior, and, when added in a 5% concentration to oil, satisfactory detergent properties.

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N-chloroamides, as well as *N,N*-dibromoamides of sulfonic acids, are widely used for the sulfamidation of aldehydes and ketones [1] and for the dipyranylation of alcohols and phenols [2]. Chloroamine-T is the best reagent for the aminohydroxylation and aminohalcogenation of alkenes [3].

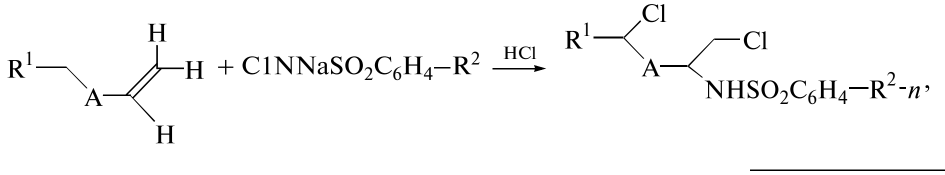
Earlier, we found [4] that the reaction between *N*-chlorosulfonamides of sulfonic acids and α-olefins results in the formation of *N*-β-chloroalkylarylsulfonamides, and the product yield depends on the nature of the medium and temperature. The direction of the addition reaction and the conditions under which a nucleophile is substituted for the chlorine atom in *N*-β-chloroalkylarylsulfonamides were studied [4]. Some of the synthesized compounds showed high anticorrosive and antioxidant activity as additives for lubricating oils.

It is known that increasing the length of alkyl radical allows compounds to form protective stable films on a metal surface, ensuring high lubricating properties [5]. Such additives improve the viscosity index, decrease the pour temperature, and reduce the corrosive activity of oil. In this connection, the synthesis of polymeric compounds containing both sulfonamide and other functional groups is of great interest.

In this work, we have studied the reaction between *N*-monochlorosulfonamides and an isobutylene–styrene cooligomer. The choice of the latter reactant was determined by the fact that isobutylene cooligomers with vinylaromatic monomers superior in stability against thermomechanical degradation to other commercial polymeric viscosity additives [6].

EXPERIMENTAL

The reaction of *N*-monochlorosulfonamides (chloroamine-B, chloroamine-CB) with isobutylene–styrene cooligomers (MW = 600–650) was carried out in the presence of HCl as described elsewhere [4]:



where R^1 is the isobutylene–styrene co-oligomer (MW = 600–650), A = $-CH_2-$ or $-CH_2CH_2-$, and R^2 = (1) H or (2) Cl.

The reactant chemicals were technical-grade chloroamine-B, chloroamine-CB, and 2,5-dibromobenzenesulfone-*N*-ethyl-*N*-chloroamide.

***N*- β-chloropolyalkylarylsulfonamide (1)**. A mixture of 65 g (0.1 mol) of co-oligomer, 35.23 (0.13 mol) *N*-sodium-*N*-chlorobenzenesulfonamide (chloroamine), and 100 ml of benzene was stirred for 20 min, and then 18.2 ml of concentrated HCl was added dropwise at a rate required for the temperature not to exceed 50°C. The resultant mixture was stirred at 50°C for 3 h, cooled, and diluted with 100 ml of hexane. The precipitate was filtered off, and the mother liquor was washed with water and dried; the solvent was evaporated. The residue, a viscous yellow product, was *N*- β-chloropolyalkylarylbenzenesulfonamide (**1**). The amount of unreacted sulfonamide (precipitate) was 4.1 g, and the product yield was 99 g (87.2%). Found, %: Cl 6.81; S 3.01; N 1.67. The molecular weight was 920.

2,5-Dibromobenzenesulfone-*N*-ethyl-*N*-chloroamide (2) was synthesized via the reaction of 2,5-dibromobenzenesulfone-*N*-ethylamide with sodium hypochlorite.

2,5-Dibromobenzenesulfone-*N*-ethylamide (100 g) was dissolved during heating in 500 ml of a 1 N solution of NaOH; then, 400 ml of 1.4 M sodium hypochlorite solution was added dropwise to the resultant mixture and the latter was stirred for 2 h. The product was filtered off and recrystallized from chloroform. The yield of 2,5-dibromobenzenesulfone-*N*-ethyl-*N*-chloroamide was 89.3 g (81.9%). bp 71–72°C. Found, %: C 25.68; H 1.96; N 4.1. Calculated, %: C 25.43; H 2.13; N 3.71.

Isobutylene–styrene co-polymer (MW = 600–650) was obtained as described elsewhere [6] by the polymerization of isobutylene and styrene in the presence of $AlCl_3$ as a catalyst.

N-β-Chloropolyalkylaryl-4-chlorobenzenesulfonamide (**2**) was prepared in a similar way via the reaction of the cooligomer with chloroamine-CB. Taken: 65 g of cooligomer and 41.1 g of chloroamine-CB. Obtained: 95 g (yield of 86.5%). Found, %: Cl 10.9 (11%); S 3.25; N 1.73.

***N*-β-Chloropolyalkylaryl-*N*-ethyl-2,5-dibromobenzenesulfonamide (3)**. The isobutylene–styrene cooligomer (65.0 g (0.1 mol)) (MW = 650) was dissolved in 100 ml of benzene. A solution of 45.3 g (0.12 mol) of *N*-chloro-*N*-ethyl-2,5-dibromobenzenesulfonamide in 100 ml of benzene was added dropwise to the resulting mixture at such a rate that the temperature did not exceed 50°C. The resultant mixture was stirred at 50°C for 2–3 h, cooled, and diluted with 100 ml of hexane. The precipitate was filtered off, and the solvent was evaporated. The residue was *N*-β-chloropolyalkylaryl-*N*-ethyl-2,5-dibromobenzenesulfonamide (**3**).The yield was 105.8 g (90%). Found, %: halogen (Cl + Br) 20.4; N 1.41.

The structure of compounds **1**–**3** was confirmed by IR data. Comparison of the spectrum of the reactant cooligomer with that of the products of its reaction with chloroamines (compounds **1**–**3**) shows the presence of new functional groups. The spectra of **1**–**3** exhibit an absorption band at $\nu = 3315–3370$ cm^{-1} corresponding to the *trans*-associated form of SO_2N and at a frequency of 3250 cm^{-1} referred to the NH group. Both of these bands are absent from the spectrum of the reactant cooligomer. The absorption bands at 1340–1350 and 1160–1170 cm^{-1}, which likewise are not displayed by the initial cooligomer, indicate the presence of the SO_2N group. The absorption bands at 640–650 and 560–580 cm^{-1} prove the presence of halogen atoms in compounds **1**–**3**.

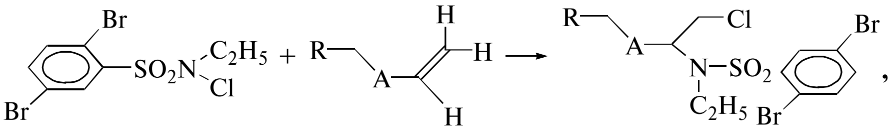
The yields of the products were determined by two methods: basing on the amount of chloroamine participating in the reaction and using a method of liquid adsorption chromatography which is applied in studying polymer additives and intermediate products [7].

The unreacted chloroamine was isolated as sulfonamide insoluble in a benzene–*n*-hexane mixture and was separated by filtration. The adsorbent used in liquid chromatography was a mixture of SiO_2/Al_2O_3 in a ratio of 9 : 1. A specimen of the test substance was dissolved in *n*-hexane and chromatographed on a column with the adsorbent using hexane as an eluent and washing the column until the substance is removed. The solvent was removed and the product was weighted. The residue in the column was washed with a benzene–isopropanol blend taken in a 1 : 1 ratio. The solvent was removed, and the residue was weighted; its amount corresponded to the unreacted product.

RESULTS AND DISCUSSION

In the study of the influence of the temperature and the time of the reaction between chloroamine-B and the cooligomer taken in an equimolar ratio, it was found that the product yield depends mainly on the reaction temperature: increasing the temperature up to 50°C increases the product yield. The further rise in the temperature increases the yield of chlorinated byproducts, and the yield of the desired product decreases. The optimal reaction time is 3 h.

According to the obtained results, the addition of *N*-alkyl-*N*-chloroarylsulfonamide proceeds easier than that of other chloroamines: the yield of the desired product reaches 90%:



(3)

The results of tests of *N*-β-chloropolyalkylarylsulfonamides

Compound	Concentration, wt %	Corrosion, g/m^2	Detergent properties according to the Papok–Zarubin–Vipper method, points
M-8 without an additive	–	180–20	5.0–5.5
1	0.5	58.8	–
	2	16.1	–
	3	10.2	2.5–3
	5	2.9	2.0–2.5
2	2	62.1	–
	5	16.3	–
	5	6.4	2.5–3
3	0.5	16.3	–
	2	7.1	–
		3.6	–
	3	0.5	2.5–3
	5		

where R is the isobutylene–styrene cooligomer and A = $-CH_2-$ or $-CH_2CH_2-$.

The anticorrosive, detergent, and tribological properties of the products of the cooligomer reactions with chloroamines (compounds **1**–**3**) were examined.

As follows from the data presented in the table, compounds **1**–**3** admixed to M-8 lubricating oil exhibit high anticorrosive activity at a concentration of 2–3% and satisfactory detergent behavior at a 5% concentration.

Studying the influence of the concentration of compound **1** (Fig. 2) on the anticorrosive properties of I-12A oil revealed that the optimal concentration for lead and copper plates was 7 and 1%, respectively. However, the addition of compound **1** makes it possible to decrease the value of corrosion to 2 g/m^2 in the case of a copper plate (data obtained for a 7% concentration of compound **1**). This finding indicates that compound **1** is a very strong copper passivator, despite the presence of the chlorine atom.

An increase in the concentration of compound **1** in I-12A oil leads to an increase in the general wear index (Fig. 3) and a decrease in the wear spot diameter.

In summary, the products of the reaction between the cooligomer and chloroamides of sulfonic acids in addition to their anticorrosive and detergent properties considerably improve the antiwear properties of

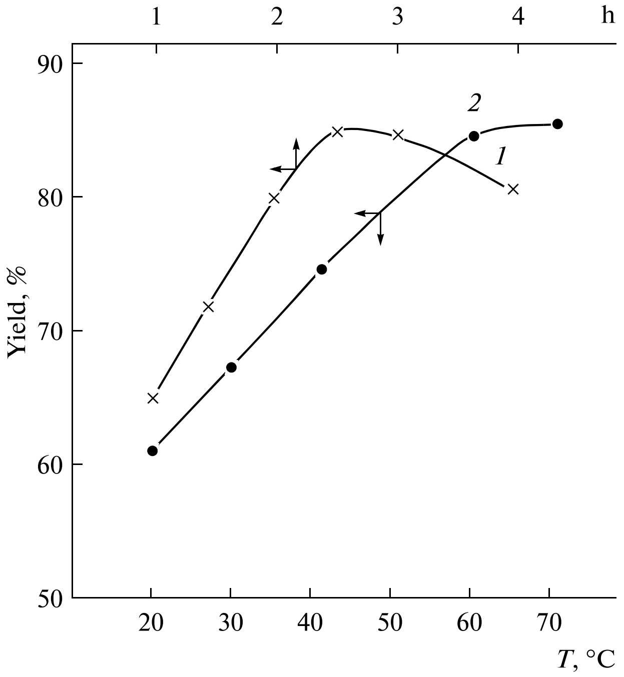


Fig. 1. Influence of the reaction (*1*) time and (*2*) temperature on the yield of the product in the reaction of *N*-chloro-*N*-sodiumbenzenesulfonamide with the isobutylene–styrene cooligomer.

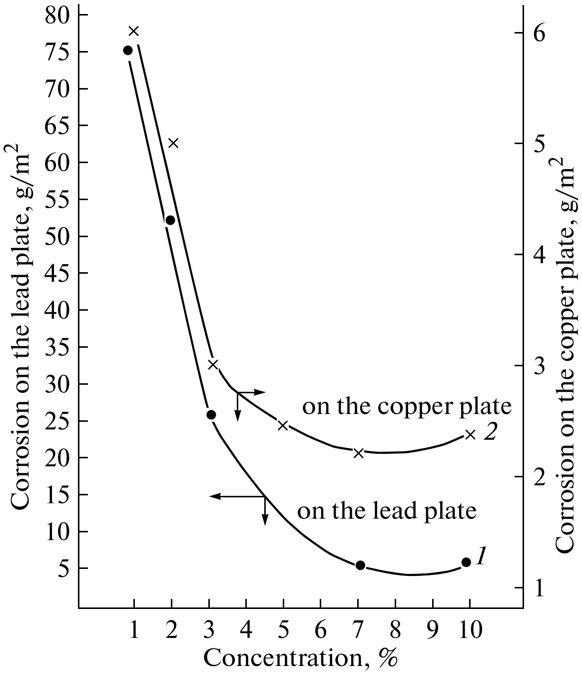


Fig. 2. Effect of the concentration of compound **1** on lead and copper plates.

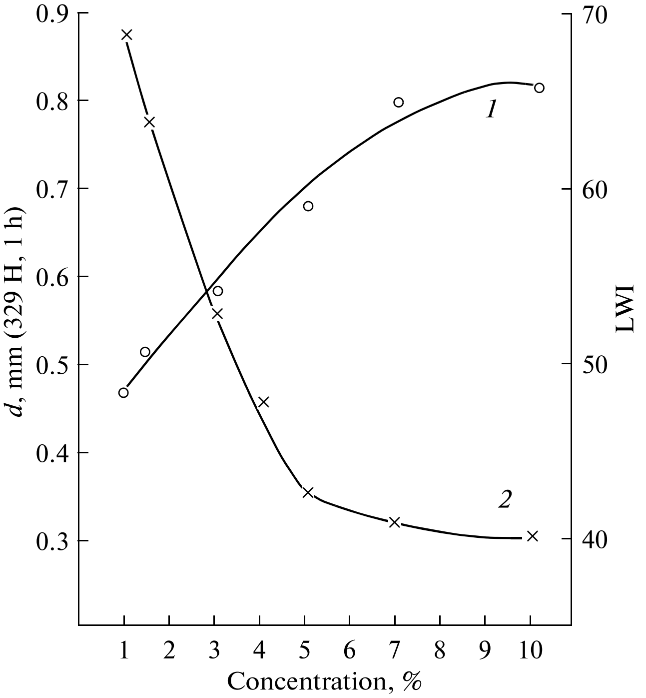


Fig. 3. Effect of the concentration of compound **1** on the (*1*) wear spot diameter and (*2*) the load wear index (LWI) for I-12A oil.

oils and, hence, are effective multifunctional additives.

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