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Technologies for producing environmentally safety oil additives

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Abstract. In the article we predetermined compounds to improve the quality of oils used in machines and mechanisms, as well as these compounds are environmentally safety. Thioamides due to their reactivity and chemical properties find wide applicability in chemical industry, engineering and agriculture. But these compounds are very less studied as additives used to improve the quality of oils used in machines and mechanisms. For this purpose, research work has been carried out to study the enhancement of anti-corrosion and anti-wear properties of additives in lubricating oils involving n-chlorophenyl thioacetamides. In this article hydraulic and lubrication properties of thioamides with respect to corrosion, corrosion, friction and thermo-oxidation properties are investigated. In order to test the effect of synthesized thioamides on their structure as additives, a number of oils were tested. In addition, the corrosion reduction of thioamides in oils has been studied and tested. The synthesized thioamides have been studied in lubricating and hydraulic oils derived from petroleum and their volume has been studied to improve the quality of thioamides in oils and their resistance to corrosion, corrosion and thermal oxidation. The article clarifies the issues involved in improving the quality of oils as a thioamide additive.

1 Introduction

Thioamides are a class of organic compounds that contain a thioamide functional group similar to an amide with a sulfur atom instead of an oxygen atom. Thioamides are thioataxes of amides.

According to their chemical features and reactivity, thioamides have found wide implementation in chemical industry, engineering, agriculture, etc. They are irreplaceable raw materials in rubber production as accelerator of vulcanization process, flotation agent, component for preservation liquids. Studies have shown that thioamides like n-chlorophenyl thioacetamide are very poorly studied as additives to improve the quality of lubricating, hydraulic and mineral oils derived from oil. The article is dedicated to the study of properties of thioamide compounds as additives for lubricating and hydraulic oils.

In order to study improvement of antiwar properties of lubricating oils for movement and friction of machine mechanisms and parts, a number of ethionamide compounds have been studied [1-2].

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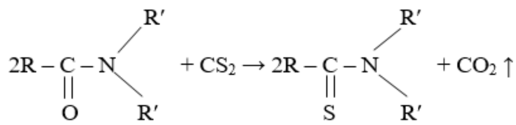
2 Materials and methods

Experimental. The drawback of these compounds is that they are not corrosion-resistant at normal temperatures. Ethionamides are added to paraffinic and complex diester oils in an amount of 5-10% as antiwear and friction agents [3]. Of these amides, N-alkyl, N-N'-dialkyl, or N-alkyl-N-alkoxy alkyl and its derivatives can be added as base oils [1-3].

N-monosubstituted thioamides are synthesised by the interaction of 2-pyrrolidone with CS_2 at high temperature and pressure and are used as additives for hydraulic oils, as vulcanisation oxidising agents and as corrosion inhibitors:



Here: R is an alkyl radical, a combination of alkyl, cycloalkyl and aryl radicals: for each R the number of carbon atoms is 1-20.

The total number of carbon atoms in the amide and thioamide ranges from 3 to 30.

n-chlorophenyl thioacetamides were synthesized by interaction of p-chloroacetophenone with sulfur. To prove the structure of the synthesized compounds, the thioamides underwent an alkaline hydrolysis reaction to give p-phenylacetic acid and further by reaction with (III) phosphorus chloride or with (V) phosphorus chloride p-chlorophenyl acetyl chloride were converted.

By the action of amines on p-chlorophenyl acetyl chlorides the corresponding amides were obtained, and then by the action of phosphorus chloride (V) converted into chlorophenyl thioacetamides [4-6]:

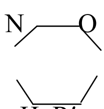
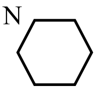
$$\text{n-ClC}_6\text{H}_4\text{C(O)CH}_3 + \text{S} + \text{HNRR}' \xrightarrow[-H_2O]{} \text{n-ClC}_6\text{H}_4\text{CH}_2\text{C(S)NRR}'$$

$$+\ \text{KOH}\downarrow\ \ \text{-NHRR}',\ \text{K}_2\text{S}$$

$$\text{n-ClC}_6\text{H}_4\text{CH}_2\text{COOH}$$

$$+\text{PCl}_5\downarrow\ \text{-POCl}_3,\ \text{HCl}$$

$$\text{n-ClC}_6\text{H}_4\text{CH}_2\text{C(O)NRR}' \xleftarrow[-HCl]{+HNRR'} \text{n-CLC}_6\text{H}_4\text{CH}_2\text{C(O)Cl}$$

Here: R = R′ = CH_3 (I); R = R′ = C_2H_5 (II); R = H, R′ = C_3H_7(III);
R = R′ = C_3H_7(IV);
R = R′ = C_4H_9 (V); NRR′ =  (VI); NRR′ =  (VII);
R = H, R′ = C_6H_5 (VIII); R = H, R′ = $CH_2C_6H_5$ (IX);
R = C_2H_5, R′ =C_6H_5 (X);
R = H, R′ = CH (CH_3)$CH_2C_6H_5$ (XI).

As a result of studies on the reaction of interaction of p-chloroacetophenone with sulfur and amines the effect of temperature and reaction rate have been studied.

It has been established, that the maximum yield of thioamides is obtained at the reaction temperature 115-120°C, at the reaction time 5.5-6 hours and at the ratio p-chloroacetophenone: sulphur: morpholine, respectively, 0.1: 0.2: 0.2.

3 Results and Discussion

The exit of the final reaction product is also influenced by the structure of the amines. The exit in the case of aliphatic and heterocyclic amines is higher compared to that of aromatic amines.

The structural structure of the synthesized thioamides was proved by IR and TMP spectra ([TMP] that is available in the PhotochemCAD package, version 2.1a [8].

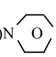
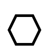
p-chlorophenyl acetoamides are white or yellowish crystalline substances. They are well soluble in acetone, benzene or ether. The purity of thioamides was determined by gas-liquid chromatography and ascertained to be 96-98%.

The constants of the thioamides are given in Table 1.

3.1 Experimental part of the synthesis of p-chlorophenylthioacetoamides.

In a round-bottom flask 15.5 g (0.1 mol) of n-chloroacetophenone, 6.4 g (0.2 mol) of sulfur and (0.2 mol) of some amine are placed. The reaction is heated for 6 hours at 115-120°C. After completion of the reaction the final product is dissolved in benzene, washed with water, dried and then after distillation of the benzene the remaining crystalline substance is crystallized in ethyl alcohol

Table 1. Constants of the synthesized p-chlorophenyl thioacetoamides.

Connect	Names of compos	Chemical formula of compounds	Exit, %	Temperature °C	Element analysis			
					Actually		Calculation	
					N	S	N	S
I	N,N- dimethyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)N(CH$_3$)$_2$	69.2	112-113	6.48	15.34	6.55	14.99
II	N,N- dimethyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)N(C$_2$H$_5$)$_2$	70.9	110-111	5.55	13.46	5.79	13.25
III	N,N- propyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)NHC$_3$H$_7$	52.0	98-99	5.98	14.54	6.15	14.07
IV	N,N- dipropyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)N(C$_3$H$_7$)$_2$	71.3	125-126	4.87	12.16	5.19	11.88
V	N,N- dibutyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)N(C$_4$H$_9$)$_2$	76.4	101-102	4.78	10.87	4.70	10.76
VI	n-chlorophenyl thiomorpholide	n-ClC$_6$H$_4$CH$_2$C(S)N 	85.5	95-96	5.35	12.60	5.46	12.53
VII	n-chlorophenylthioacetopiperide	n-ClC$_6$H$_4$CH$_2$C(S)N 	87.3	80-81	5.35	12.87	5.52	12.63
VIII	N- phenyl-n-chloropheny lthioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)NHC$_6$H$_5$	68.5	122-123	5.49	12.30	5.35	12.25
IX	N- ethyl-N-phenyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)NHCH$_2$C$_6$H$_5$	61.8	118-119	5.16	11.84	5.07	11.62
X	N- ethyl-N-phenyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)N(CH$_2$)C$_6$H$_5$	54.0	108-109	4.60	10.89	4.89	11.05
XI	N-(β-phenyl)isopropyl-n-chlorophenyl thioacetamide	n-ClC$_6$H$_4$CH$_2$C(S)NHCHCH$_2$C$_6$H$_5$ CH$_3$	72.3	75-76	4.42	10.69	4.61	10.55

3.2 Synthesis of p-chlorophenyl acetic acid.

In a round bottom flask a 25% solution of potassium hydroxide with water (2.5 g KOH+10ml H_2O) is prepared. Then 24.2 g (0.1 mol) of p-chlorophenyl thioacetomorpholide is added and heated for 8-10 hours. It is then neutralized with hydrochloric acid. The crystals of p-chlorophenyl acetic acid are dried after filtration.

3.3 Synthesis of p-chlorophenyl acetyl chloride.

After dissolving 20.8 g (0.1 mol) of phosphorus chloride (V) in 100 ml of dichloroethane and adding in portions 17.1 g (0.1 mol) of p-chlorophenyl acetic acid heats to 83°C (to the boiling point of dichloroethane) for 3 hours under constant stirring. After distillation of the solvent the product is crystallized in benzene.

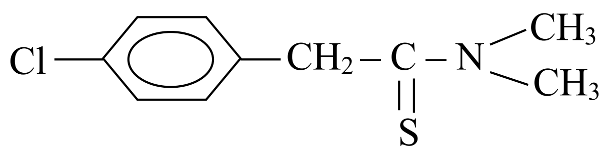
3.4 Synthesis of p-chlorophenyl acetamides.

In a three-necked flask 18.9 g (0.1 mol) of p-chlorophenyl acetyl chloride was placed in the presence of benzene and at 0 - (+2)°C, and 0.2 mol of corresponding amine was added from dropping funnel a and stirred for 35 minutes. Then 50-60 mL of ammonia water are added to the reaction mixture. The reaction mixture is washed several times with water and filtered. After distillation the solvent is crystallized in ethyl alcohol.

Synthesis of p-chlorophenyl thioacetamides by interaction of phosphorus chloride (V) with p-chlorophenyl acetamide [4-6].

To a 0.1 mol solution of p-chlorophenyl acetamide in boiling benzene 5.6 g (0.025 mol) phosphorus chloride (V) is added in small portions. The reaction product is stirred for 3.0-3.5 h in boiling benzene. After the end of the reaction the product is washed with water, distilled over benzene and crystallized in ethyl alcohol.

N, N- dimethyl-p-chlorophenylthioacetamide.



Initial components:

- p-chloroacetophenone − 15.5 g (0.1 mol)
- sulphur − 6.4 g (0.2 mol)
- dimethylamine (32%) − 28.2 g (0.2 mol)

Exit: 14.8 g (69.2); T_{pd} = 122-123°C
In fact: % content N − 6.48
% content S − 15.34
Calculated: % content N − 6.55
% c content S − 14.99
Figures 1 and 2 show the effect of temperature and reaction time on the thioamide yield.

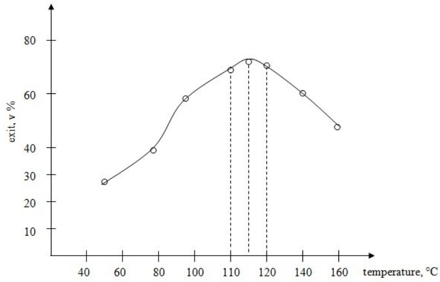


Fig. 1. Influence of temperature on the thioamide yield (p-chloroacetophenone: sulphur: morpholine), for 6 hours.

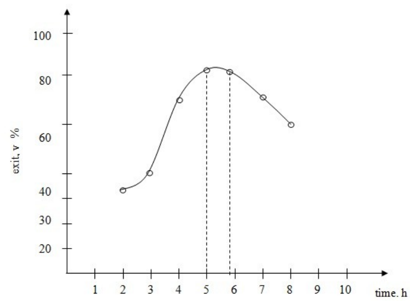
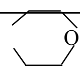
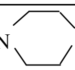


Fig. 2. Influence of the reaction time on the product yield (p-chloroacetophenone: sulphur: morpholine), (115-120°C).

Table 2. Influence of p-chlorophenyl thioacetamide on corrosion rate in oils.

No.	**Examples**	**Additive content per 100 g oil**		**Velocity of corrosion g/m^2·h.**
		mol	**g**	
1	Lubricating oil	-	-	180-200
2	oil + n – $ClC_6H_4CH_2C(S)N(CH_3)_2$	0.002 0.005 0.007	0.43 1.07 1.50	6.5 1.2 1.0
3	oil + n – $ClC_6H_4CH_2C(S)NH – C_3H_7$	0.002 0.005 0.007	0.46 1.14 1.59	14.7 7.6 5.5
4	oil + n – $ClC_6H_4CH_2C(S)N(C_4H_9)_2$	0.002 0.005 0.007	0.60 1.49 2.09	13.1 8.4 5.3
5	oil + n – $ClC_6H_4CH_2C(S)N$ O	0.002 0.005 0.007	0.51 1.28 1.79	4.3 3.2 2.1
6	oil + n – $ClC_6H_4CH_2C(S)N$	0.002 0.005 0.007	0.51 1.27 1.78	5.3 3.3 2.2
7	oil + n – $ClC_6H_4CH_2C(S)NHC_6H_5$	0.002 0.005 0.007	0.52 1.31 1.83	6.4 3.2 2.3
8	oil + n – $ClC_6H_4CH_2C(S)N(C_2H_5)C_6H_5$	0.002 0.005 0.007	0.58 1.45 2.03	1.0 1.0 0.8
9	oil + n – $ClC_6H_4CH_2C(S)NHCH(CH_3)CH_2C_6H_5$	0.002 0.005 0.007	0.61 1.52 2.13	12.7 3.1 2.2

Table 3. Effect of p-chlorophenyl thioacetamides on increasing the thermal-oxidative stability of oils.

No.	Examples	Additive content per 100 g oil		Sediment, in %	Increased viscosity
		mol	g.		
1	Lubricating oil	-	-		10.30
2	oil + n – $ClC_6H_4CH_2C(S)N(CH_3)$	0.002 0.005 0.007	0.43 1.07 1.50	3.20 5.17 5.61	28.90 26.61 29.91
3	oil + n – $ClC_6H_4CH_2C(S)NHC_3H_7$	0.002 0.005 0.007	0.46 1.14 1.59	3.10 3.86 4.76	20.32 22.70 26.31
4	oil + n – $ClC_6H_4CH_2C(S)N(C_4H_9)_2$	0.002 0.005 0.007	0.60 1.49 2.09	2.82 3.01 4.21	18.12 21.42 24.15
5	oil + n – $ClC_6H_4CH_2C(S)N$ 	0.002 0.005 0.007	0.51 1.28 1.79	6.17 12.70 5.93	21.31 28.42 29.33
6	oil + n – $ClC_6H_4CH_2C(S)N$ 	0.002 0.005 0.007	0.51 1.27 1.78	3.31 4.62 5.01	19.42 26.34 28.28
7	oil + n – $ClC_6H_4CH_2C(S)NHC_6H_5$	0.002 0.005 0.007	0.52 1.31 1.83	1.83 2.04 3.81	13.01 14.16 18.81
8	oil + n – $ClC_6H_4CH_2C(S)N(C_2H_5)C_6H_5$	0.002 0.005 0.007	0.58 1.45 2.03	2.02 1.14 2.82	16.24 19.20 19.90
9	oil + n – $ClC_6H_4CH_2C(S)NHCHCH_2C_6H_5$ | CH_3	0.002 0.005 0.007	0.61 1.52 2.13	0.45 1.20 1.40	10.13 15.08 17.21

4 Conclusion

The capabilities of thioamides (p-chlorophenyl thioacetamides) as anti-corrosion, anti-wear, (thermo-oxidative) additives in hydraulic and lubricating oils have been tested.

In order to check the influence of the structure of synthesised thioamides on their effectiveness as additives, compositions of 100 g oil with the addition of 0.002; 0.005; 0.007 mol of the substance, respectively, were prepared (Table 3). As a result, it was found that the corrosion rate in hydraulic and lubricating oils decreases from 180-200 g/m^2-h to 0.8-31.2 g/m^2-h. For a 10 g/m^2h reduction in corrosion rate, the thioamides examined must have a content of 0.005 mol in 100 g of oil. In thioamides, changing the nitrogen atom radical has little effect on their ability to reduce the corrosion rate. For example, if adding 0.002 mol of p-chlorophenyl thioacetomorpholide to 100 g of lubricating or hydraulic oil reduces the corrosion rate by 4.3 $g/m^2/h$, in the case of N,N-dimethyl-p-chlorophenyl-thioacetamide this figure will be 6.5 $g/m^2/h$ and N-phenyl-p-chlorophenyl-thioacetamide - 6.4 $g/m^2/h$.

Secondary and tertiary amine additives with the same alkyl radical have the same ability to reduce corrosion rates. Thioamides with a phenyl radical are more effective additives in terms of their thermo-oxidative capacity than those with alkyl and heterocyclic radicals. For example, if 0.002 mole of N-(β-phenyl) isopropyl-p-chlorophenyl thioacetamide is added to oils, no precipitate occurs in the oxidised oil, the viscosity increase is 10.13%. Whereas when 0.002 mol of p-chlorophenyl thioacetomorpholide and N,N-dimethyl-p-chlorophenyl thioacetamide were added to the oils, 6.17 and 21.31 precipitates and viscosity increase of 3.20% and 28.9% respectively are obtained (Tables 2 and 3).

- P-chlorophenyl thioacetamides were synthesized by the interaction of p-chloroacetophenone with sulphur and various amines as well as carboxylic acid chloralhydrates with phosphorus chloride (V) with amines.
- The structures of the synthesized compounds were proved by IR and PMR spectroscopy.
- The synthesized thioamides are applied to lubricating and hydraulic oils as additives and are found to improve oil properties as well as increase resistance to corrosion, friction and thermal oxidation.
- Synthesized thioamides are recommended for use in oils as additives to improve their properties.

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