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Methods for Producing Kaptax and Improving the Environmental Safety of Its Production

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Abstract

Known laboratory-scale and industrial methods are reviewed therein concerning the production of one of the most important vulcanization accelerators such as kaptax (2-mercaptobenzothiazol) those are based on modifying the substituents in the thiazol ring and synthesizing from acyclic precursors. The latter include also the main industrial method of obtaining kaptax based on the reaction between aniline, sulphur and carbon disulphide dangerous from the environmental point of view. Potentialities are demonstrated concerning the development of methods for producing kaptax without using carbon disulphide, which would significantly improve the environment safety of the process.

Key words: kaptax, obtaining, production

Contents

INTRODUCTION

Benzothiazols represent one of the most important groups of rubber vulcanization accelerators. So, according to the authors of [1], the production of benzothiazols in the USA in 1990 was equal to 25.4 t, *i. e.* about 80 % of all the vulcanization accelerators produced. In Russia, the production of vulcanization accelerators based on benzothiazol amounted to about 5 t in 2005 [2]. Among the vulcanization accelerators of this group, there is 2-mercaptobenzothiazol (kaptax, MBT).

Kaptax is for long being used in industry as a rubber vulcanization accelerator. Although a recent trend is observed that consists in crowding kaptax out of the market of vulcanization accelerators by sulphenamides [3], it remains an important compound in this segment of the chemical industry, since kaptax represents the production an intermediate product in manufacturing the sulphenamides. In addition, the kaptax is much cheaper than sulphenamides, so it is widely used in rubber compositions based on natural rubber, synthetic rubber and latex mixtures undemanding with respect to the regime of processing, and as an independent or secondary accelerator. Kaptax is also used as a reagent in the analytical chemistry of heavy metals [4].

In Russia, the production of vulcanization accelerators based on benzothiazol (including kaptax) is developed at the Volzhskiy Orgsintez JSC (Volzhskiy City, Volgograd Region)

[3, 5, 6]. However, the volume of the production does not meet the needs of the rubber industry, therefore a part of the product is supplied from abroad.

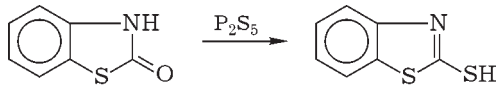
The traditional process for obtaining kaptax is based on the reaction between aniline, carbon disulphide and sulphur [1]. Significant disadvantages of this reaction consist in the use of fire hazardous and toxic carbon disulphide, the presence of malodorous gaseous emissions (hydrogen sulphide, *etc.*) and waste water containing sodium sulphate, which results in a serious burden on the environment. In connection with the fact, of relevant importance is a development of novel technologies for producing MBT and improvement of existing ones in order to implement (create) a more environmentally safe method for obtaining thereof.

All the known methods of the preparation of 2-substituted benzothiazols (including kaptax) could be divided into the two groups [4]: 1) modifying the substituents at the position 2 of the thiazol ring, 2) synthesizing the thiazol ring from precursors belonging to the benzene series.

MODIFICATION OF SUBSTITUENTS IN THE THIAZOL RING

Obtaining the MBT in this way is possible either from oxybenzothiazol 2, or from 2-halogenated benzothiazols [4]. The latter, in turn, could be prepared either from 2-oxybenzothiazol *via* the reaction with appropriate phosphorus or sulphur oxyhalides such as $POHal_3$ and $SOHal_2$, or from 2-aminobenzothiazol according to Sandmeyer reaction [4, 7]. 2-Bromobenzothiazol can also be obtained using the reaction between benzothiazol and N-bromosuccinimide [8, 9] or immediately with bromine at 450 °C [10].

2-Oxybenzothiazols usually exist in a tautomeric form **I** with a hydrogen atom at the nitrogen atom. The substitution of oxygen therein to yield the MBT (**II**) is possible *via* the reaction with P_2S_5 [4]:



I **II**

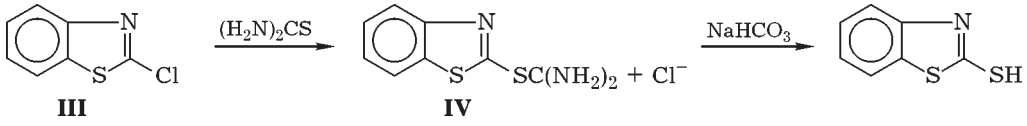
The nucleophilic substitution of a halogen atom in the position 2 of benzothiazol proceeds relatively readily. In order to obtain pure 2-mercaptobenzothiazol (yield 80 %) from chloro derivative **III** it is appropriate to use the reaction with thiourea in boiling ethanol (the formation of the isothiouronium salt **IV**) followed by the treatment with an aqueous solution of sodium carbonate [8, 11] (Scheme 1).

Using sodium hydrocarbonate instead of hydrochloric acid for decomposing the isothiouronium salt causes the yield of MBT to be reduced down to 28 % [12].

There are other ways of halogen substitution by the thiol group.

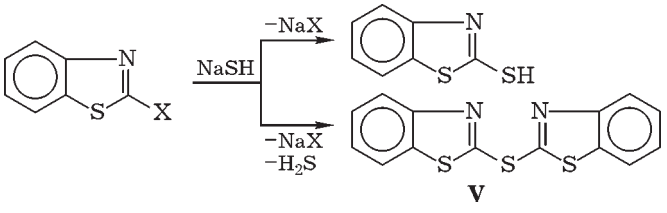
1. Performing the reaction with the hydrosulphide of an alkali metal. As a by-product there can be formed corresponding sulphide **V**, whereas disulphide formation is observed in the presence of air [13] (Scheme 2).

2. Performing the reaction between halogenobenzothiazols and thiosulphate ion to form *S*-benzothiazolyl thiosulphate **VI** and subsequent acid-catalysed hydrolysis [14] (Scheme 3).



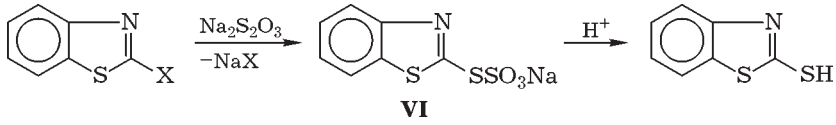
III **IV**

Scheme 1.



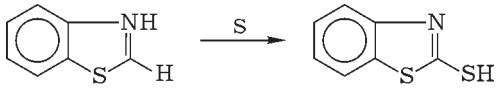
V

Scheme 2.



Scheme 3.

The group of techniques for the modification of substituents in the side chain of the thiazol ring could be supplemented with a method of MBT obtaining *via* the reaction between unsubstituted benzothiazol **VII** and elemental sulphur proposed in [15]:



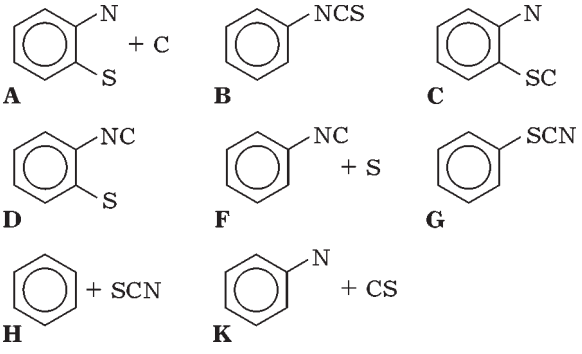
VII

This reaction is conducted at an atmospheric pressure and at the temperature ranging within 230–250 °C. The optimal ratio between the reagents is equal to 0.95–1.1 mol of sulphur per 1 mol of benzothiazol. The MBT yield is equal to 91.5 % with respect to benzothiazol. Unsubstituted benzothiazol is a by-product of industrial MBT synthesis from aniline, carbon disulphide and sulphur, thereby its reaction with sulphur could be used to increase the yield of MBT in the industrial process.

All of the listed methods for producing MBT require for preliminary obtaining other substituted benzothiazols.

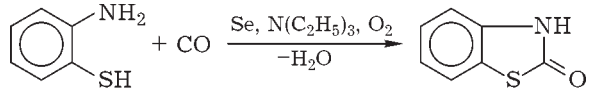
SYNTHESIZING THE THIAZOL RING FROM PRECURSORS BELONGING TO BENZENE SERIES

Below there are presented all theoretically possible ways of constructing the benzothiazol ring from benzene derivatives [4]:



All these methods for the synthesis of benzothiazols are described in the literature, except for types **G** and **H** [8, 16].

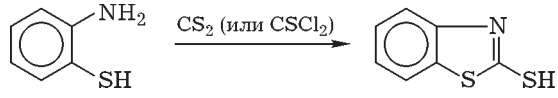
Method A. 2-Oxybenzothiazol is formed from *o*-aminothiophenol **VIII** with the yield equal to 64 % *via* treating it with a solution of carbon monoxide CO in the presence of triethylamine and selenium, and further treating with oxygen [17, 18]:



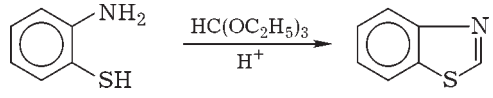
VIII

The reaction proceeds at a room temperature and atmospheric pressure, dimethylformamide (DMFA) being used as a solvent. Oxygen treatment of the reaction solution is necessary for the regeneration of the elemental selenium. Selenium in this method could be used either in the equimolar or in the catalytic amounts. In the latter case, the carbon monoxide is bubbled through the reaction mixture together with oxygen. At the end of the process only oxygen is supplied [18].

o-Aminothiophenol reacts also with carbon disulphide under boiling in ethanol or with thiophosgene $CSCl_2$ in chloroform at a room temperature to form the MBT [4, 19]. Just in this way the kaptax was for the first time obtained in 1887 [13, 20]:



The reaction between *o*-aminothiophenol and 1,1,1-trietoxymethane (ethyl orthoformate) can be used to produce unsubstituted benzothiazol with a 85 % yield [21, 22]:



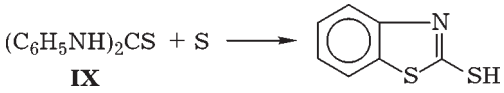
o-Aminothiophenol could be obtained *via* the reaction between *o*-nitrochlorobenzene and sodium disulphide or sodium hydrosulphide followed by reducing di-*o*-nitrophenyl disulphide with zinc in acetic acid [20]. There is possibility [23] of a direct reduction of *o*-nitrochloroben-

zene by sodium hydrosulphide (Na_2S + H_2S mixture) to yield *o*-aminothiophenol. The combination between this reaction and the reaction of *o*-aminobenzenethiol with carbon disulphide allows obtaining MBT from *o*-nitrochlorobenzene with the yield amounting to 84 % [23] through one stage. There is *o*-chloroaniline formed as a by-product.

o-Aminothiophenol could be prepared either from aniline *via* the action of S_2Cl_2 followed by reducing in an alkaline medium or through the reduction of para sulphonic acid [20]. However, the best preparative method for the synthesis of *o*-aminothiophenol is considered to consist in the hydrolysis of commercial MBT by concentrated alkali solution [4].

Free *o*-aminothiophenols are readily oxidized to produce disulphides even when stored in air, so in the reactions of synthesis one should use freshly prepared *o*-aminothiophenol or its salt. Because of the instability of *o*-aminothiophenols and the feasibility of obtaining *o*-aminothiophenols from MBT (a target product of our study) the synthesis of MBT from *o*-aminothiophenol is seldom used in the laboratory practice.

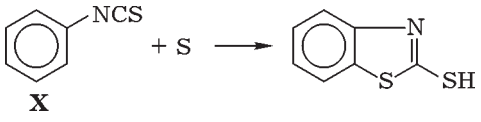
Method B. The MBT could be formed from N-arylthioamides, arylthioureas, isothiocyanates and arylthiocarbamates with a 74 % yield *via* heating N,N'-diphenylthiourea **IX** with sulphur at temperature values higher than 200 °C [24–26]:



In this reaction, there is 2-(phenylamino)-benzothiazol observed as a by-product to be formed. The overall yield of these two benzothiazols is equal to 90–96 % with respect to theoretical one. The authors of [25] attributed the formation of two products to the fact that compound **IX** is in tautomeric equilibrium with respect to pseudothiourea $C_6H_5N{=}C(SH)NHC_6H_5$ which can exist both in the syn and anti forms. The latter react with elemental sulphur in a different manner: the syn form produces MBT *via* aniline cleavage, whereas the anti form yields 2-(phenylamino)-benzothiazol *via* cleaving hydrogen sulphide.

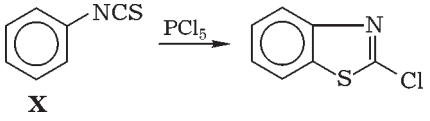
Phenylisothiocyanate **X** could be converted into benzothiazols in two ways:

a) the action of sulphur at 250 °C thereon to form the MBT [27]:

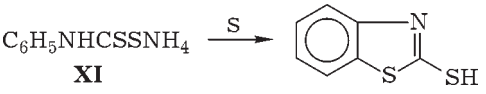


The process is carried out under pressure at a temperature of 220–225 °C in the presence of water, or salt hydrates; the yield being equal to 88–92 % whereas the purity level is equal to 98 %.

b) the action of PCl_5 thereon at 170 °C to form 2-chlorobenzothiazol with a 15 % yield [4, 24]:



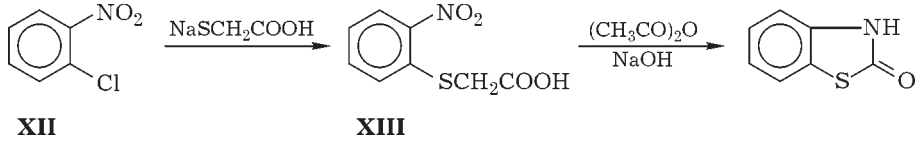
The ammonium salt of dithiocarbamic acid **XI** under heating with sulphur at a temperature of 224 °C is converted into MBT with the yield equal to 74 % [4, 25]:



Zinc dithiocarbamate reacts in a similar way [25]. Salt **XI** could be prepared from aniline, carbon disulphide and ammonia [25].

Method C. Obtaining from the *o*-nitrochlorobenzenes and thiocarboxylic acids [4]: the treatment of *o*-nitrochlorobenzene **XII** by sodium thioacetate results in the formation of corresponding nitrophenylthioacetic acid **XIII** that after treating by acetic anhydride and alkali is cyclised to give 2-oxybenzothiazol (Scheme 4).

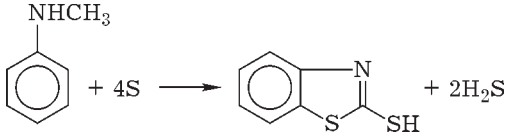
Method F. In this case, MBT is prepared from sulphur and anilides. The application of



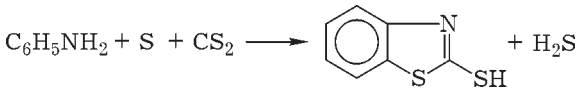
XII **XIII**

Scheme 4.

this method is limited because satisfactory yield is observed in a number of cases only. So, the yield of MBT from the interaction between formanilide and sulphur under heating is equal to only 46 % [28]. In a similar manner, one can obtain kaptax (with the yield ranging 50–60 % with respect to theoretical one) from N-methylaniline and elemental sulphur [29]. The reaction is performed within the temperature range of 22–275 °C under a pressure of 62 atm:



Method K. Obtaining from aniline, carbon disulphide and sulphur [25, 30, 31] *via* the following reaction:



First, this method was proposed by Kelly in 1926 [30, 31]. The reaction between aniline, carbon disulphide and sulphur takes place at the temperature values up to 280–285 °C and elevated pressure (up to 150 atm). The yield is equal to 85 %. On the basis of this reaction an industrial process was proposed for obtaining kaptax (Kelly process) which is the main way to obtain MBT by now [1, 32].

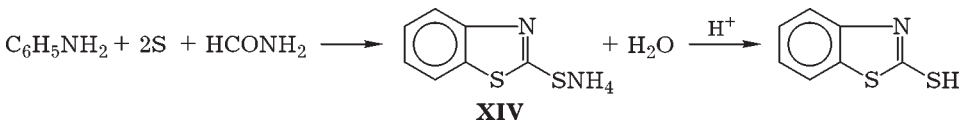
This reaction results in the fact that alongside with hydrogen sulphide and MBT there are impurities observed to yield such as N,N'-diphenylthiourea, 2-(phenylamino)-benzothiazol, benzothiazol, 2-methylbenzothiazol, phenyl isothiocyanate, *etc.* [33–36]. The kaptax formed is purified by dissolving in alkali to separate from insoluble resinous impurities with further acidifying the kaptax salt solution by a mineral acid.

Improving the performance of the process, in particular increasing the yield of MBT (up to 96 %) could be performed *via* the extraction of the resinous impurities by organic solvents (toluene, *etc.*) and via further mixing the extraction products with the initial reagents (recycling) [see, *e. g.*, 37, 46]. As raw materials, it is proposed to use either nitrosobenzene with hydrogen sulphide in a mixture with aniline [46], or a mixture of aniline and nitrobenzene with carbon disulphide [36]. To all appearance, one could use also other aniline precursors, for example azobenzene [20].

Carbon disulphide represents a fire hazardous and toxic substance (flashpoint amounting to −30 °C, flammability limits ranging within 1.25–50 vol. %, the MPC in the air of the operation zone amounts to 1 mg/m^3, the third class of danger [47]), wherewith attempts were made to replace this substance by formamide [28] or DMFA [48]. In this case, the reaction between formamide, sulphur and aniline is carried out under superatmospheric pressure at a temperature of 190 °C. First, the ammonium salt of MBT **XIV** is obtained, wherefrom the final product is formed *via* acidifying with a mineral acid with 86 % yield as calculated for aniline reacted (the amount of unreacted aniline was not reported in [28]), melting point being of 158–159 °C (for pure MBT melting point is equal to 181–182 °C) (Scheme 5).

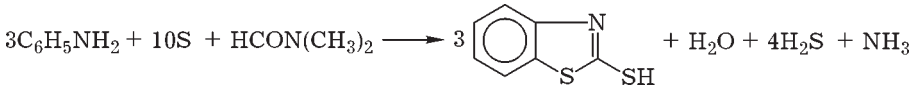
2-Mercaptobenzothiazol was obtained (with a 66 % yield with respect to theoretical value) *via* the reaction between aniline, sulphur and DMFA at 250 °C under a pressure equal to 62 atm (Scheme 6).

Finally, the MBT with the yield ranging within 30–80 % with respect to the theoretical

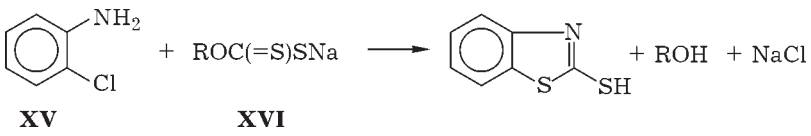


XIV

Scheme 5.



Scheme 6.



XV **XVI**

Scheme 7.

value could be obtained *via* the reaction between aniline, sulphur and secondary amine (*e. g.* dimethylamine) or thiuram sulphide containing the CH_2 group in the side chain, within the temperature range of 225–275 °C at a pressure equal to 53 atm [49]. This process usually requires for an excess of aniline (50–500 %).

It is assumed that formamide, dimethylformamide and substances containing the CH_2 group give initially carbon disulphide *via* the reaction with sulphur, which carbon disulphide further reacts with aniline and sulphur in a common manner.

All of the methods for obtaining MBT from aniline with no use of carbon disulphide exhibit a low yield of the target product, whereas the product formed is not pure to a sufficient extent.

Recently [50], a method for obtaining MBT was proposed based on the reaction between halogenoaniline **XV** and dithiocarbonate an alkali or alkaline earth metal **XVI**, or carbon disulphide in the presence of alcoholic solutions of alkalis (Scheme 7).

According to [50], the reaction is carried out at an atmospheric pressure within the medium of DMFA at 140–150 °C in an inert atmosphere (nitrogen), which results in the formation of MBT with net yield amounting to 95 %. As far a solvent is concerned, this process could involve also other high boiling dipolar aprotic solvents such as dimethyl sulphoxide or dimethylacetamide. The reaction could involve various dithiocarbonates (R can vary within a wide range), but it is preferable to use compounds wherein R is presented by lower alkyls, since these compounds are available on an industrial scale as flotation reagents. Usually the reaction requires for using an excess of dithiocarbonate. The mentioned reaction is also applicable with respect to other *o*-halogenoanilines, especially those with electron-accepting substituents in the benzene ring [51]. Table 1 demonstrates data concerning the MBT yield inherent in obtaining with the use of this reaction under different conditions [50].

This method allows avoiding a direct operation with carbon disulphide due to the use of ready-made dithiocarbonates, however in the industry the latter are prepared using just the same carbon disulphide.

CATALYTIC METHODS FOR PRODUCING KAPTAX

All of the above described methods for obtaining kaptax are non-catalytic ones. The first example of the catalytic process for kaptax obtaining from aniline, carbon disulphide and sulphur in the presence of a catalyst such as diarylaminodithiophosphoric acid (10 mol. % with respect to initial reagents) is described in [52]. Later, the authors of [53] proposed a way to reduce the process time by 75 % *via* the use of such catalysts as red phosphorus or metallic mercury. However, in connection with environmental aspects, this method found no practical application. A background work in this field is

TABLE 1

Effect of reaction conditions on the yield and purity in MBT in the reaction between dithiocarbonate and *o*-chloroaniline at 150 °C

Dithiocarbonates	Aniline/dithiocarbonate molar ratio	Solvent*	Time, h	Yield, %	$T_{m.p.}$, °C
$C_2H_5COS_2Na$	1 : 3	DMFA	12	94.6	179–180
i-$C_4H_9COS_2Na$	1 : 3	DMSO	12	95.2	179–181
i-$C_4H_9COS_2K$	1 : 2	DMAA	20	93.8	178–180

* DMFA – demethylformamide, DMSO – dimethyl sulphoxide, DMAA – dimethylacetamide.

TABLE 2

Comparing the efficiency of catalysts in the Kelly process at 230 °C and the reaction duration of 3.5 h [54]

Catalysts (concentration, %)	Mass fraction of catalyst against the starting reagent, %	Kaptax yield with respect to aniline, %
–	–	69.7
HCl (37)	0.3	86.0
HBr (50)	4.7	91.7
I_2	5.9	90.3
H_3PO_4 (85)	5.0	78.2
$AlCl_3$	1.2	90.9
Aluminium silicate	13.2	85.2
Montmorillonite	10.0	84.6
Silicoaluminium phosphate	16.3	84.0

considered to be presented by a patent [54], whose authors suggested using homogeneous catalysts (Lewis and Brønsted acids, halogens), as well as solid acid catalysts such as zeolites in the amount of 0.2–30 mass % with respect to the substrate, as catalysts in the Kelly process. Table 2 presents comparative data from the authors of [54] for a non-catalytic reaction and the reaction and in the presence of different acidic catalysts. It is seen that different acids exert a catalytic effect in the Kelly process.

To compare the effect of the acid nature on the parameters of the Kelly process in dynamics, Table 3 presents data concerning a variety of organic acids and sulphuric acid (the conditions being analogous to those given in Table 2, but the catalyst loading was calculated with respect to aniline).

One can see that also in this case each acid used results in accelerating the reaction.

However, the regeneration of a homogeneous acidic catalyst is difficult, this procedure requires an increase in alkali consumption at the stage of MBT extraction to result increasing the amount of mineral waste.

Table 4 presents the characteristics of different ways to obtain the MBT. It could be seen that the highest MBT yield values are reached using methods 2, 3, 11 and 18. Obtaining the MBT from benzothiazol as well as from other 2-substituted benzothiazols represents a multistage process. Owing to a higher cost of nitrosobenzene and *o*-chloroaniline as compared to aniline and to the necessary of applying an organic solvent in the case of *o*-chloroaniline, the Kelly process still remains the main industrial method for obtaining the MBT (kaptax), despite all its disadvantages.

As already mentioned, the main drawback of the Kelly process consists in use fire haz-

TABLE 3

Comparing the efficiency of different Kelly process catalysts in dynamics [54]

Catalysts	Mass fraction of catalyst against aniline, %	Kaptax yield with respect to aniline, % Process duration, h		
		1	2	3.5
–	–	13.4	37.6	69.7
p-Toluenesulphonic acid	5.5	49.7	64.4	ND
Methanesulphonic acid	8.5	48.0	53.3	ND
Trichloroacetic acid	6.4	ND	ND	89.8
50 % H_2SO_4 solution	4.7	ND	ND	80.6

Note. ND – no data.

TABLE 4

Comparison of different methods for obtaining MBT

Exp. No.	Reagents	*T*, °C	*P*, atm	Time, h	Medium	Yield, %
1	Aniline, CS_2, and S, with no resin recycling	250	75	3	–	85.6
2	Aniline, CS_2, and S, with resin recycling	250	75	3	–	96.3
3	Nitrosobenzene, H_2S, CS_2	245	72	0,5	–	96.4
4	Aniline, nitrobenzene, CS_2*	130–250	6.5	6*		
5	Phenylisothiocyanate, S	220–250	>1	1.5–2.5	up to 5 % H_2O	88–92**
6	Aniline, formanilide and S	190	>1	6	–	86
7	Formanilide and S	240	>1	3	–	46
8	Aniline, $HCON(CH_3)_2$ and S	250	62	3	–	66
9	N-methylaniline and S	250	62	5	–	60
10	Aniline, S and $NH(CH_3)_2$	250	53	3	–	81
11	*o*-Chloroaniline, $C_2H_5COS_2Na$	150	1	13	$HCON(CH_3)_2$, nitrogen atmosphere	94.6
12	2-Chlorobenzothiazol, thiourea	78	1	ND	Ethanol	80
13	2-Oxybenzothiazol, P_2S_5		1	ND	–	ND
14	*o*-Aminothiophenol, CS_2	78	1	8	Ethanol	ND
15	*o*-Aminothiophenol, $CSCl_2$	25	1	ND	$CHCl_3$	ND
16	Aniline, CS_2, NH_3, S (or heating $C_6H_5NHCSSNH_4$ with S)	224	>1	1.5	–	74
17	$(C_6H_5NH)_2CS$, S	265	>1	4	–	74
18	$(C_6H_5NHCSS)_2Zn$, S	247	>1	1.8	–	77.5
19	Benzothiazol, S	230–250	1	3.3	–	91.5
20	*o*-Nitrochlorobenzene, NaSH, CS_2	100	1	20	H_2O	84

Notes. 1. dash – with no solvent. 2. ND – no data.

* Including for 1 h at 130 °C, 1 h at 145 °C, 1 h at 160 °C, 3 h at 250 °C.

** The yield of crude (non-purified) product.

ardous and highly toxic carbon disulphide. From Table 4 it is seen that the process of obtaining kaptax could be performed with no use of carbon disulphide (methods 5–10, 18), although the product yields would be lower in this case (80–91.5 %) in comparison with an industrial process (96 %). However, the raw material that is used in these methods (dimethylformamide, N-methylaniline and dimethylamine) is easily accessible, since all these compounds are produced by the domestic industry [4]. Thus, there is a potentiality of searching for better MBT synthesis conditions on the basis of these three substances with no use of carbon disulphide. Hydrogen sulphide formed in these processes is to a significant extent less dangerous as compared to carbon disulphide. This substance has a narrower range of ignition (4.5–45.5 vol. % *vs.* 1.25–50 vol.% inherent in carbon disulphide), it does not exhibit self-ignition in atmospheric air; the MPC value of H_2S in an operation zone being 10 times higher than the MPC value inherent in CS_2 [47]. Furthermore, the hydrogen sulphide as against the carbon disulphide has many efficient purification ways developed, including those with obtaining useful products (see, for example, [55]).

CONCLUSION

2-Mercaptobenzothiazol (kaptax) represents an efficient vulcanization accelerator for natural and synthetic rubbers, a feedstock for the synthesis of other important vulcanization ac-

celerators. For this reason it is still in demand in the rubber industry. The traditional methods for obtaining kaptax belong to environmentally hazardous industries, since the process is carried out using carbon disulphide that represents a fire-hazardous and toxic raw material. In this connection it is appropriate to develop new processes for obtaining kaptax with no use of carbon disulphide. One could consider, for example, processes based on dimethylformamide, N-methylaniline or dimethylamine as feedstock to be promising for the further development.

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