

# Methods for Obtaining and Prospects of Developing an Up-to-Date Low-Waste Production of Guanamines in Russia

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## Abstract

Known laboratory-scale and commercial methods for obtaining guanamines (6-alkyl or aryl substituted 2,4-diamino-1,3,5-triazines) based on modifying substituents in the triazine ring as well as on synthesizing them from acyclic precursors are described. It has been demonstrated that the most convenient method for obtaining guanamines is nowadays represented by the reaction between dicyandiamide and nitriles in the presence of a strong base, employing high-boiling alcohols as solvents. The reaction conditions are considered in detail, data concerning its kinetics and to the mechanism are presented. The conditions for commercial employing the reaction are described allowing one to develop an up-to-date low-waste technology for obtaining high quality guanamines.

**Key words:** guanamines, obtaining, manufacture

## INTRODUCTION

Guanamines (6-alkyl and aryl substituted 2,4-diamino-1,3,5-triazines)  $RC_3N_3(NH_2)_2$  are of interest as raw material for manufacturing polymers (guanamine-formaldehyde resins) [1–3], as components for so-called antipyrenes (fire-retardant additives) [4, 5] and metal corrosion inhibitors [6]. Moreover, some guanamines exhibit pronounced biological activity [7]. So, it was demonstrated that some 6-aryl-2,4-diamino-1,3,5-triazines promote healing peptic ulcer-

ation [8, 9] as well exhibit anti-inflammatory activity [10], whereas a number of guanamines show antiallergenic [11] and diuretic [12] activity.

Nowadays abroad guanamines are being commercially produced. Their application is mainly similar to melamine (2,4,6-triamino-1,3,5-triazine employed for obtaining melamine-formaldehyde resins and fire-retardant additives), though to a more limited extent [1–3]. In the industry there are first of all benzo ( $R = C_6H_5$ ; 6-phenyl-2,4-diamino-1,3,5-triazine)- and aceto ( $R = CH_3$ ; 6-methyl-2,4-diamino-1,3,5-triazi-

ne)-, as well as phenylaceto ( $R = C_6H_5CH_2$ ; 6-benzyl-2,4-diamino-1,3,5-triazine)-, stearo ( $R = n-C_{17}H_{35}$ ; 6-*n*-heptadecyl-2,4-diamino-1,3,5-triazine)- and capry ( $R = n-C_7H_{15}$ ; 6-*n*-heptyl-2,4-diamino-1,3,5-triazine)guanamines used [2, 3]. The most part of guanamines are used for manufacturing aminoformaldehyde (amine) resins, as usual in the form of copolymers with melamine (for example, from the mixture of benzoguanamine with melamine at a ratio of (0.2–0.3) : 1). In addition, guanamine-formaldehyde resins are used as hardeners for polyester (alkyd and acryl) resins. Guanamine-formaldehyde resins demonstrate a number of advantages with respect to other amine resins [1]: 1) a slower formation and hardening; 2) a higher resistance of their solutions with respect to the influence of acids (so, for the resin obtained from acetoguanamine one can observe the gel formation in 10 % hydrochloric acid to occur in 7 days, whereas for that based on melamine this process occurs within several hours); 3) a higher elasticity, impact strength, stability to decrepitation stability and water resistance of hardened products. Moreover, resins based on guanamines in the course of time evolve to a considerable extent less formaldehyde as compared to melamine-based ones. Low resistance against UV radiation represents a disadvantage of resins based on benzoguanamine [2].

The areas of application of guanamine-formaldehyde resins are manifold [2, 3]: 1) in the electrical industry they are used as a component of insulating coatings; 2) in the furniture industry these compounds are employed for manufacturing decorative paper-laminated plastics (high-pressure laminates); 3) in the textile industry they are used in order to wrinkle resistance and water repellency to cloths; 4) in the tanning industry they are used in order to give solvent stability to skins and leather; 5) in the manufacture of plastic crockery; 6) for costing rolled metal and tins; 7) in making decorative panels for automobiles; 8) as a main component of fluorescent pigments. A small part of guanamines is used as combustion retardants (for example, acetoguanamine cyanurate [13, 14]). The action of these compounds is based on the fact that under decomposing guanamines there is gaseous nitrogen evolved to absorbed

heat. Capryguanamine represents one of the best stabilizers of formaldehyde solutions [15].

The production of resins on the basis of guanamines is carried out by such large-scale companies as CYTEC Industries (the USA, CYMEL aminorubber) and BASF (Germany, Luwipol aminorubber). Japanese Nippon Shokubai Co. produces benzoguanamine since 1964. In the last few years the manufacture of melamine and guanamines is developed in China (such companies as CAC Group of Hong Kong, Shanghai Nanda Chemical Plant, *etc.*).

As far as the Soviet Union is concerned, there was an industrial production manufacture of benzoguanamine in Baku. However, at the present moment there is no industrial-scale production not only of guanamines, but even of melamine in Russia. Melamine is supplied to Russia from abroad, although carbamide obtained in great amounts could be employed as a raw material for the manufacture of the former. In 2008 it was decided to develop melamine production facilities at the Nevinnomysskiy Azot JSC (Nevinnomyssk City) [16]. There are no data available in the accessible literature concerning the demand for guanamines in the Russian market. At the same time, taking into account that the demand for guanamines is lower as compared to the melamine requirement, one could estimate an upper limit. So, the demand for melamine in Russia in 2005 was estimated approximately equal to 25 thousand (for the manufacture of melamine-formaldehyde resins) [17], whereas its double growth is predicted to be by 2015. When taken into account that the ratio between the consumption of guanamines as copolymers and melamine is equal to ((0.2–0.3) : 1) the upper limit of the demand could be estimated to amount to 5–7 thousand ton per year.

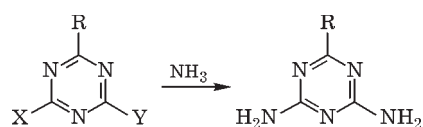
In connection with the aforesaid it is of interest to consider known laboratory-scale and industrial methods for obtaining guanamines and potentialities for developing their up-to-date and low-waste production facilities in Russia.

Guanamines could be obtained either by means of modifying substituents in the triazine ring or *via* forming the triazine ring from acyclic precursors [18, 19].

### MODIFYING SUBSTITUENTS IN THE TRIAZINE RING

The synthesis guanamines by modifying substituents in the triazine ring is possible with the use of the nucleophilic substitution reaction in corresponding 6-alkyl(aryl)-triazines [20], or the reduction of 6-alkyl(aryl)-2,4-dinitro compounds [20], or the reaction between diamides of triazinedicarboxylic acids and sodium hypobromite [20]. Data concerning the obtaining of guanamines *via* the latter method are not available from the literature, whereas the reduction of nitro compounds is of no practical importance, since nitrotriazines are obtained, in turn, via the oxidation of aminotriazine [20].

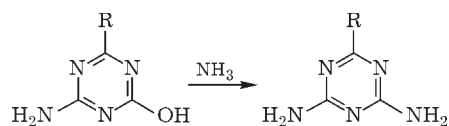
Carrying out the reaction of nucleophilic substitution in the triazine ring usually is of no difficulty. Possible ways to synthesize guanamines via the mentioned method are demonstrated below:



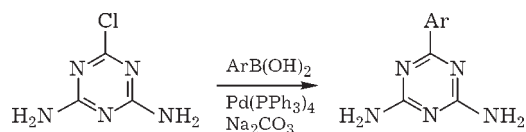
X, Y – halogen (Hal), CHal<sub>3</sub>, NO<sub>2</sub>, OH

The substitution of both chlorine atoms in dichlorotriazines readily occurs at the temperature ranging within 70–100 °C in the presence of an alkaline agent, for example soda [21]. The trihalogenomethyl group can be also readily substituted [20].

However, the substitution of the hydroxy group requires for providing rather severe conditions. So, 6-substituted 2-amino-4-hydroxytriazines react with ammonia under pressure at 250–500 °C to form target guanamines [22]. The yields of guanamines resulted from this method amounts to 30–80 % as compared to the theoretical yield:

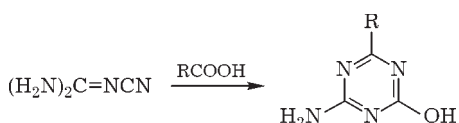


Furthermore, recently it has been established that arylguanamines could be obtained with a good (70–77 %) yield via boiling 2,4-diamino-6-chloro-1,3,5-triazine with arylboric acids within 1,2-dimethoxyethane medium in the presence of a Pd complex [23]:



The general disadvantage of the method for modifying the substituents in the triazine ring consists in the fact that the initial derivatives of triazine can usually be obtained only via multistage synthesis. In the case of the aforementioned reaction, in addition the synthesis of arylboric acids is required.

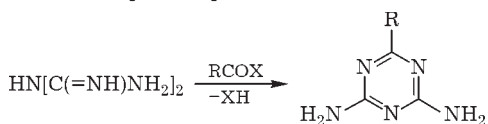
Rather readily, by means of dicyandiamide condensation with carboxylic acids, only 6-substituted 2-amino-4-hydroxytriazines can be formed [22]:



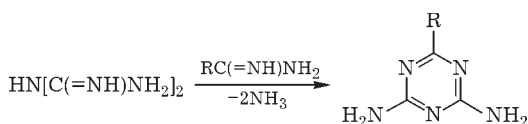
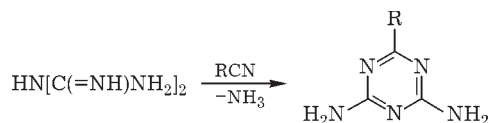
### SYNTHESIZING GUANAMINES FROM ACYCLIC PRECURSORS

It is theoretically possible to perform the synthesis of the six-membered triazine ring from molecular fragments 5 + 1, 4 + 2, 3 + 3 and 2 + 2 + 2 [18]. The following methods are known for obtaining guanamines from acyclic precursors:

1. Synthesis from biguanidine and from the derivatives of carboxylic acids (from molecular fragments 5 + 1). Researchers use to employ, as such derivatives, ethers, halogen-containing anhydrides, anhydrides, nitriles and amidines [24–30]:



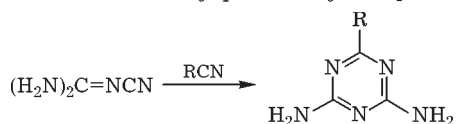
X – halogen, OR', R'COO



In the case of biguanidine reactions with the esters of carboxylic acids a good yield of guanamines can be achieved in the presence of an alkaline agent such as sodium hydroxide or methoxide. In order to realize these reactions the reagents are exposed to infusion in an alcoholic solution at a room temperature within several hours. In the case of biguanidine reac-

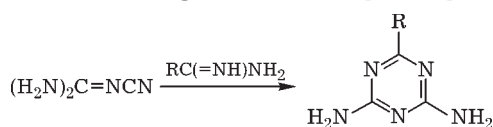
tion with halogen-containing anhydrides of carboxylic acids one can obtain guanamines with a good (80 % and higher) yield with the use of sodium carbonate as an acceptor of acid. As initial compounds one can use biguanidine salts, too (for example, sulphate), in this case the reaction is performed in the presence of NaOH.

2. From dicyandiamide *via* the reaction with nitriles (from molecular fragments 4 + 2) with the yields of 90 % and higher as compared to the theoretically possible yield [31–33]:

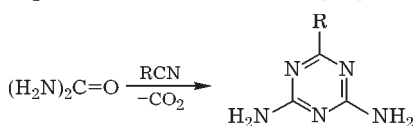


This reaction is used for industrial obtaining guanamines; it is described in detail in the following section.

3. From amidines and dicyandiamide (from molecular fragments 3 + 3) [26, 34]:

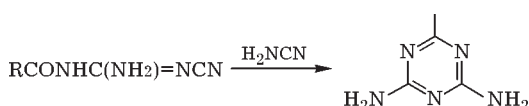


4. From nitriles and ureas at 250–500 °C in liquid ammonia medium [35]:



In this case dicyandiamide is replaced by more available urea. However, this method requires for complicated equipment (in order to create a high pressure of ammonia), whereas the quality of products formed is low.

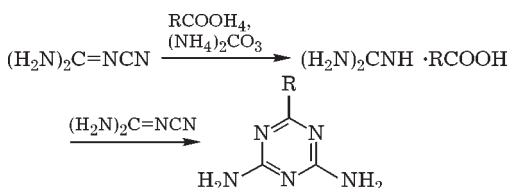
5. From acyldicyandiamide and cyanamide [36]:



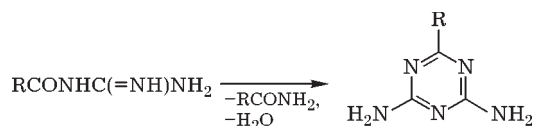
Acyldicyandiamide is obtained through the reaction of dicyandiamide with corresponding chloroanhydride in the presence of aqueous NaOH solution at a room temperature. Further the acyldicyandiamide obtained is treated by an aqueous solution of cyanamide at the temperature of 90 °C. After cooling the solution the guanamine obtained is separated by means of filtering.

6. Pyrolysis of guanidine salts. For the first time guanamines have been obtained *via* this method [26], however their yield was low. More-

over, the reaction proceeds only with the salts of those aliphatic acids whose number of carbon atoms is no more than six. A modification of this method was proposed where guanidine salts obtained *in situ* from dicyandiamide, ammonium salt of corresponding carboxylic acid and ammonium carbonate react (without solvent) with the excess dicyandiamide at 180–215 °C [37] to form guanamines with a good yield:

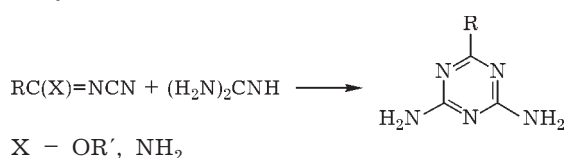


7. Heating acylguanidines at 190–210 °C without solvent with the yield of 40–95 % [38]:



Acylguanidines can be obtained from guanidine and the esters carboxylic acids [38].

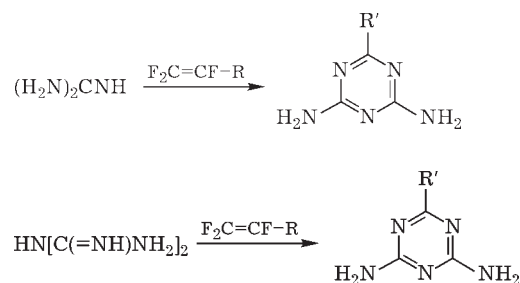
8. From guanidine and N<sup>2</sup>-cyanoamidines or N-cyanoimidates:



The syntheses of benzo- (with the yield of 19 % comparing to the theoretical one) and acetoguanamines (the yield of 53 % as compared to the theoretical one) from corresponding N<sup>2</sup>-cyanoamidines [39] as well as the synthesis of acetoguanamine from N-cyanoacetimidate (the yield of 77 % with respect to the theoretical yield) [40] are described in the literature. The reaction with N-cyanoamidines is carried out under boiling the solution of initial reagents in methanol; the reaction with N-cyanoimidates is performed in methanol medium at a room temperature.

Initial N<sup>2</sup>-cyanoamidines are formed from corresponding amidines *via* the reaction with monosodium salt of cyanamide [39]. Methyl- and ethyl-N-cyanoacetimidates are formed resulting from of the interaction between acetoimidate hydrochloride with cyanamide in the medium of corresponding alcohol [40].

9. From fluoroalkenes and guanidine or biguanidine one could obtain fluoroalkylguanamines[41, 42]:



R = F, Cl, CF<sub>3</sub>, R' = CF<sub>2</sub>H, CFC1H, CF<sub>3</sub>CFH, respectively

Guanidine and biguanidine react with fluoroalkenes in dimethylformamide to form fluoroalkylguanamines. The reaction between guanidine and perfluoroethene [41] proceeds at 50–

60 °C, whereas with the other fluoroalkenes it occurs at –5...–15 °C, and the yield of fluoroalkylguanamines decreases from 100 to 20 % in going from perfluoroethene to perfluoropropene due to resinification. Fluoroalkenes react with biguanidine [42] in dimethylformamide medium at 60–70 °C to produce fluoroalkylguanamines. The yields of guanamines in this reaction are also reduced in going from perfluoroethene to perfluoropropene (from 85 to 20 % comparing to the theoretical yield) due to resinification.

Table 1 demonstrates comparative data on obtaining benzo- and acetoguanamines by means of various methods. One can see that the best parameters were obtained in the synthesis of guanamines from nitriles and dicyandiamide, which provided a high yield of a high quality product with no application of pressure. Due to this fact the present method is also used

TABLE 1

Comparison of various methods for obtaining benzo(R = C<sub>6</sub>H<sub>5</sub>)- and aceto(R = CH<sub>3</sub>) guanamines

R	Method*	M. p., °C	Yield, %	Solvent	T <sub>react</sub> , °C	Catalyst	Reaction time, h	P, atm
C <sub>6</sub> H <sub>5</sub>	1	215–8	–	–	–	–	–	1
C <sub>6</sub> H <sub>5</sub>	2a	222	83	Acetone	0–5	–	–	1
C <sub>6</sub> H <sub>5</sub>	2b	–	16	–	–	–	–	1
C <sub>6</sub> H <sub>5</sub>	3a	224–5	93	2-Methoxyethanol	125	KOH	5	1
C <sub>6</sub> H <sub>5</sub>	3b	225	70	–	–	–	–	1
C <sub>6</sub> H <sub>5</sub>	3c	224–6	–	Water	90	–	1/3	1
C <sub>6</sub> H <sub>5</sub>	10	–	80	–	400	–	2	13.6
C <sub>6</sub> H <sub>5</sub>	4	216–224	67	Liquid ammonia	300	–	2	13
C <sub>6</sub> H <sub>5</sub>	6	219–223	19	Methanol	65	–	6	1
CH <sub>3</sub>	5	–	Up to 80	–	300–400	–	2	13.6
CH <sub>3</sub>	3a	274.5	85.5	DMSO	110–130	KOH	2.25	1
CH <sub>3</sub>	3d	–	91	–	180–215	–	–	1
CH <sub>3</sub>	1	252–5	–	–	190–210	–	–	–
CH <sub>3</sub>	2c	265	61	Water : acetone (35 : 140)	5–7	NaOH	–	1
CH <sub>3</sub>	3a	271–3	96.5	2-Methoxyethanol	125	KOH	6	1
CH <sub>3</sub>	3b	–	65–70	–	–	–	–	–
CH <sub>3</sub>	4	–	–	Liquid ammonia	350	–	2	15
CH <sub>3</sub>	6	275–6	53	Methanol	65	–	6	1
CH <sub>3</sub>	7	276–7	77	Methanol	25	–	0.5	1

Note. Methods of obtaining: 1. Heating acylguanidine [26]. 2a. From biguanidine and acylchloride [26]. 2b. From biguanidine and amidine [26]. 2c. From biguanidine and anhydride of carboxylic acid [26]. 3a. From dicyandiamide and nitrile [26]. 3b. From dicyandiamide and amidine [26.] 3c. From acyldicyandiamide and cyanamide [26]. 3d. From dicyandiamide, ammonium salt of carboxylic acid and ammonium carbonate [26]. 4. From urea and nitrile [26]. 5. From 2-amino-4-hydroxytriazine and ammonia [26]. 6. From guanidine and N<sup>2</sup>-cyanoamidine [39]. 7. From guanidine and N-cyanoimidate [40].

in commercial production of guanamines. Moreover, initial substances used in the realization of other methods are either less available (for example, biguanidines obtained from dicyandiamide as well as amidines usually obtained from nitriles [43]), or obtaining them requires for multistage synthesis.

#### DICYANDIAMIDE REACTION WITH NITRILES

##### *Reaction conditions*

The aforementioned reaction between dicyandiamide and nitriles with the formation of guanamines has industrial application, therefore just this reaction has been investigated in detail; various modifications were proposed for this method with the purpose of improving the yield and the quality of the target product [31, 32, 44–56].

It has been demonstrated that carrying out the reaction requires for using a solvent (usually any alcohol) and a catalyst. With no catalyst the reaction occurs only under pressure at the temperature higher than 200 °C [31]. Moreover, the yield of the product in this case to a considerable extent depends on the purity nitrile used.

It was revealed [44] that the reaction is catalyzed by bases such as caustic alkali [32], potash, piperidine [44], *etc.* When alcohols are employed as solvents one could use metal potassium and sodium those reacting with alcohols tend to form corresponding alcoholates. It is most preferable to use caustic potassium or sodium as a catalyst. Employing weaker bases results in a decrease in the yield of guanamines [50].

Owing to not sufficiently high temperature of the process the use of methanol or ethanol as a solvent [45] the yields of guanamines, as a rule, are insignificant (for example, the yield of benzoguanamine amounts to only 25 % with respect to theoretically possible one).

In order to obtain a high yield (higher than 90 % comparing to theoretical one) in methanol or ethanol medium one should perform the process under pressure adding liquid ammonia [46]. It is possible to use pure liquid ammonia as a solvent (and a base) within the temperature range of 0–120 °C [47, 48] under pressure. Yields of the product in this case can amount up to 90 % and more. The disadvantage of employing pure liquid ammonia as a

solvent consists in the necessity to provide a high operating pressure for three process (at 100 °C the pressure amounts up to 61 atm [49]). The use of mixed solvents (methanol or ethanol + ammonia) allows one to lower the operating pressure of the process. The operating pressure of the process could be varied changing the ratio between alcohol and ammonia [49].

As a solvent it is more preferable to employ high-boiling alcohols such as 2-methoxy and 2-ethoxy ethanol (methyl or ethyl cellosolve) [32, 50, 57–65]. Other high-boiling alcohols are also used, for example, 1-pentanol [51]. In the case of aliphatic nitriles with more than eight carbon atoms the yield of corresponding guanamines in cellosolve media was low; therefore it has been proposed to use dimethylsulphoxide (DMSO) as a solvent [52–54]. This allows one to increase the yield of the product up to 90 % and more.

Recently a communication has appeared [55] concerning the application of ionic liquids (salts of imidazolium cation liquid at a room temperature) as a solvent in the reaction between dicyandiamide with nitriles. Performing the reaction with a number of aromatic nitriles in the medium of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]) in the presence of KOH under microwave (MW) irradiation at 130 °C the authors obtained corresponding guanamines with the yield of 70–87 %. The time of the reaction amounted to only 10–15 min, whereas for usual solvents the reaction duration ranges from several hours to one day. An important role in this case was played by microwave irradiation [55, 56]; without the latter the reaction time abruptly increased, and the yield of the product was reduced. However, employing this method could result in overheating the reaction mixture, since ionic liquids are non-volatile. In order to prevent the reaction mixture from overheating it was proposed to use a computer-controlled source of microwave radiation, which has allowed researchers to perform the process at an almost constant temperature [55].

In separate cases other solvents could be applied. So, in obtaining phosphor-containing guanamines [66] (promising fire-retardant additives) from phosphites, substituted acrylonitriles and dicyandiamide, anhydrous dioxane has appeared the most efficient as a solvent.

TABLE 2

Solvent and catalyst effect on the yield of benzoguanamine in dicyandiamide reaction with benzonitrile

No.	Solvent	Catalyst	T, °C	Time, h	P, atm	Yield, %
1	–	–	200–230	3	7	60*
2	Excess of nitrile	Pyperidine	191	3	1	85
3	Methanol	CH <sub>3</sub> ONa	65	7	1	25
4	2-Methoxyethanol	KOH	125	5	1	93
5	Methanol : ammonia (2 : 1)	NaOH	85–90	1	<18	96
6	1-Penthanol	KOH	140	24	1	78
7	MW, [BMIM][PF <sub>6</sub> ]	KOH	130	0.2	1	87
8	[BMIM][PF <sub>6</sub> ]	KOH	130	8	1	79
9	MW, 2-methoxy-ethanol	KOH	125	0.25	1	76
10	MW, [BMIM][PF <sub>6</sub> ]	Ba(OH) <sub>2</sub>	130	0.2	1	54

\*Maximal value is presented. The yield is varied depending on the initial benzonitrile purity.

Table 2 demonstrates data concerning the influence of a solvent and a catalyst in the reaction between dicyandiamide with benzonitrile.

#### Reaction kinetics and mechanism

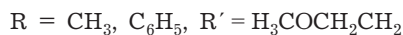
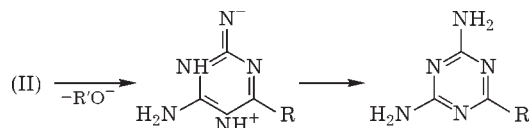
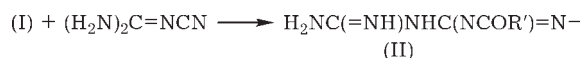
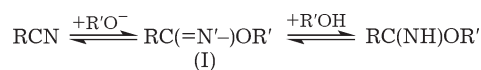
Reaction kinetics for the interaction of aceto- and benzonitriles with dicyandiamide in the presence of KOH has been investigated with the help of UV spectrophotometry [67, 68]. So, the authors of [67] have found that the reaction rate for benzonitrile in 2-methoxyethanol medium linearly depends on the concentrations of dicyandiamide and nitrile. In spite of the fact that there is a considerable scatter of points forming the reaction rate dependence on alkali concentration, which results in an imperfectly straight line plotted, the authors of [67] have found this dependence to be linear. Thus, the authors of [67] obtained the following equation for benzonitrile and dicyandiamide reaction rate:  $v = k[\text{dicyandiamide}][\text{C}_6\text{H}_5\text{CN}][\text{KOH}]$ . They have also demonstrated that the addition of cyanamide to the reaction mixture causes the reaction rate to decrease, which decrease prevents the possibility of triazine formation due to joint trimerization of benzonitrile and cyanamide that can be formed from dicyandiamide according to such reaction as



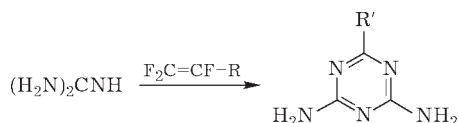
A possible mechanism for dicyandiamide reaction was proposed, which includes fast re-

versible proton abstraction from dicyandiamide and the formation of an anion. Slow anion addition to benzonitrile promotes obtaining an acyclic product that undergoes cyclization to form the triazine ring [67].

However, later, studying the kinetics of the reaction between acetonitrile [68] and dicyandiamide (in the presence of KOH) in 2-methoxyethanol medium, the same authors revealed that the reaction rate dependence on alkali concentration could be more precisely described by such relationship as:  $v \sim [\text{KOH}] (a + b [\text{KOH}])$ , where  $a$  and  $b$  are constants. The reaction rate dependence on nitrile and dicyandiamide concentration in this case remained linear, too. Furthermore, the authors investigated the kinetics acetonitrile reaction with dicyandiamide in the mixture of DMSO with 2-methoxyethanol of various composition (with the content of DMSO amounting to 70 and 80 %). It has been found that in this case the reaction rate depends only on the concentration of nitrile, but not dicyandiamide. Basing on data obtained in [68] the authors have rejected the mechanism they suggested earlier to propose a new, much more probable mechanism of the reaction: first, an addition of alkoxide ion (formed from 2-methoxyethanol and KOH) to nitrile occurs with the formation of imino ether anion (I) being in equilibrium with imino ether. Further the imino ether anion (I) undergoes addition to dicyandiamide according to the following reaction scheme



The change in the reaction order in going from 2-methoxyethanol to the mixture of DMSO and 2-methoxyethanol the authors explain by the fact that in the presence of DMSO the reaction rate is determined by such a stage as



and does not depend any more on the concentration of dicyandiamide.

#### *Industrial conditions for dicyandiamide reaction with nitriles*

In the industry, in order to obtain aceto- and benzoguanamines, people usually apply the reaction between dicyandiamide and corresponding nitriles in the presence strong alkali (KOH, NaOH) with the use of methyl or ethyl cellosolve as a solvent [1]. The reaction of dicyandiamide with nitriles is exothermic to a considerable extent (for benzonitrile  $Q = 146.2$  kJ/mol [47]), therefore after preliminary heating the mixture of reagents up to 100–120 °C and starting the reaction an intense heat removal is required (otherwise a blowout of the mixture from a reaction vessel is quite possible). The heat removal can be achieved due to solvent boiling as well as employing a powerful backflow condenser. The organization of a good heat removal from the reaction zone is of especial urgency with the use of large-scale reagent loading.

It was revealed [69] that with the use of initial reagent loading into a reactor amounting to 100 gallons (near 378 L) in volume and more, the yield of guanamines decreases. So, in the case of benzoguanamine the yield is reduced up to 60 %, whereas the color of the product formed is less-than-perfectly white, which is

undesirable in obtaining plastics. In this connection it was proposed for the case of high-scale loadings either to add dicyandiamide by several portions [69], or to fractionally enter the catalyst (alkali) [70]. Due to this fact researchers succeeded in obtaining the product of a high white purity with a good (not less than 92 %) yield, in adjusting heat-evolution rate, as well as in decreasing the overall reaction time (from 6 to 4 h) for benzoguanamine [69, 70] for the case of fractional adding the alkali.

Guanamines are not readily soluble in cellosolves, therefore they could be isolated by means of simple filtering. The solvent could be regenerated from the filtrate after separating the precipitate of guanamines via simple distillation, which allows one to minimize the amount of contaminated wastes as well as provides a low-waste quality of the technology under consideration.

#### **RAW MATERIALS FOR MANUFACTURING GUANAMINES AVAILABLE IN RUSSIA**

As it follows from all the aforesaid, raw material for industrial-scale production of guanamines is presented by nitriles, dicyandiamide, methyl (or ethyl) cellosolve and caustic alkali. Nowadays in the territory of Russia there are methyl and ethyl cellosolve (Caprolactam Plant of the Sibur-Neftekhim JSC, Dzerzhinsk; Khimprom JSC, Kemerovo) and caustic alkalis produced commercially. There is no industrial-scale production of dicyandiamide, it is mainly produced in small batches or delivered from China. As far as the nitriles are concerned (aceto-, benzo-, phenylaceto-, stearo- and caprynytriles), only acetonitrile is commercially produced in Russia (for example, at the SaratovOrg-Synthez Co., as well as by a few number of companies as a laboratory chemical reagent). Other aforementioned nitriles are not produced on an industrial scale in Russia (only in small packing, for example, benzonitrile) or supplied from abroad.

#### **CONCLUSION**

Guanamines (as usual, in the mixture with melamine) represent a promising raw material



for manufacturing various polymers (first of all amine resins) and flame resistant coatings. Basing on the analysis of literature data one may conclude that nowadays the most efficient (including in the industry) method for obtaining guanamines consists in synthesizing from dicyandiamide and nitriles in the presence of a basic catalyst, allowing researchers to obtain the products with a high (up to 90 % and more) yield having a high product quality and a minimum amount of production waste.

In order to organize an up-to-date low-waste commercial production of guanamines in the territory of the Russian Federation it is required either to purchase abroad dicyandiamide and nitriles (except for acetonitrile), or to develop a domestic production facilities for manufacturing these substances. The annual guanamine requirement for the Russian market could be estimated to range within several thousand tons.

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