MELAMINE AND DERIVATIVES OF MELAMINE

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I. INTRODUCTION

A. General

Melamine (2,4,6-triamino-1,3,5-triazine) was first prepared over one hundred years ago by Liebig (105) by heating potassium thiocyanate with ammonium chloride. It was subsequently obtained by various workers by heating guanidine carbonate or thiourea (37, 46, 97, 132, 161) or by heating cyanamide or dicyandiamide (45, 50, 51, 61, 65, 158, 168, 171). It forms a particularly stable heterocyclic structure, and it is often the principal final product of a variety of fairly high temperature reactions based ultimately on the reaction between ammonia and carbon dioxide. In the last twenty-five years its reaction with formaldehyde to give first methylol derivatives and ultimately thermosetting resins has been intensively studied, and melamine itself has therefore become a product of large-scale manufacture and use.

The manufacture of melamine on the large scale is based on heating dicyandiamide (1, 4, 75, 165) or urea (2, 54, 60, 138) in the presence of ammonia, the overall reactions being, respectively:

$$3C_2H_4N_4 \xrightarrow{\text{heat}} 2C_3H_6N_6$$

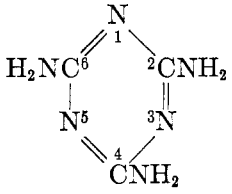
$$\underset{\text{Urea}}{6CO(NH_2)_2} \xrightarrow{\text{heat}} \underset{\text{Melamine}}{C_3H_6N_6} + 3CO_2 + 6NH_3$$

The present review does not deal in any way with the technology of melamine production or of melamine resins. Its scope covers derivatives of melamine in which there are substituents in the amino groups, whether such derivatives have

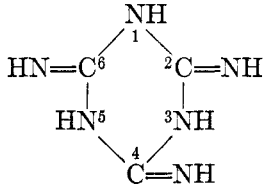
been prepared from melamine itself or not, and also derivatives of melamine (such as hydrolytic products) which are obtained directly from melamine. No such products have as yet found large-scale industrial use, but such applications as have been made or have been proposed are indicated.

B. Nomenclature

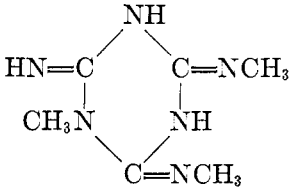
The literature is inconsistent in regard to the numbering of substituents in the melamine nucleus. Frequently the three amino positions are designated N, N′, and N″. A preferable system, which has frequently been used and which will be adopted in this report, is to follow the numbering 1 to 6, as for triazine itself, and to designate the extranuclear nitrogens as N^2-, N^4-, and N^6. This system also applies to isomelamine derivatives, substituents on the nuclear nitrogens then being in the 1-, 3-, and 5-positions.



Melamine



Isomelamine



N^2, N^4, 5-Trimethylisomelamine

II. MELAMINE

A. Some physical properties of melamine

Melamine crystallizes from water in colorless monoclinic prisms. Complete crystallographic specifications have been given (155). It has only low solubility in water and common solvents, a saturated aqueous solution at 20°C. containing less than 1 per cent of melamine, and one at 90–100°C. under 5 per cent. Chapman and others (34) made accurate determinations of the solubility of melamine in water over a range of temperatures and found the equation:

$$\log (\text{solubility}) = -1642/T + 5.101 \text{ g./100 g. water}$$

Its solubility in glycol, pyridine, and glycerol is about the same as in water; melamine is difficultly soluble in alcohol and is insoluble in inert solvents (117). It is difficultly soluble in liquid ammonia at room temperature, and at −33°C. largely separates out (62).

When heated, melamine sublimes with some decomposition. Sublimation under reduced pressure has been studied (see table 1) and the degree of decomposition measured (117).

Other physical properties of melamine are given in table 2.

The ultraviolet absorption spectrum of melamine in aqueous solutions has been examined at a range of pH values (42, 47, 49, 70, 93, 100, 101). In acid solution (pH 1.2–2.8) melamine has a peak of low intensity at 263 mμ. Study

TABLE 1

The sublimation of melamine under reduced pressure

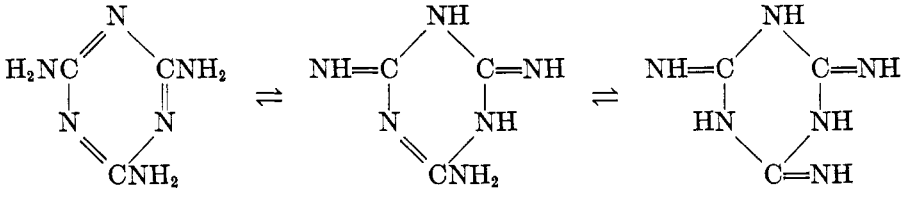
Pressure	First Sublimation Bath Temperature	Rapid Sublimation Bath Temperature	Moles of NH_3 per Hour per 100 Moles of Melamine
mm.	°C.	°C.	*moles*
3	190	280	0.38
23	210	290	0.50
50	220	300	0.56
196	250	320	1.77
772	270	330	2.5

TABLE 2

Some physical properties of melamine

Property	Value	References
Melting point	354°C.	(98, 137, 178)
Specific gravity at 25°C.	1.57	(102)
Specific heat (0–80°C.)	0.352 cal./gram	(140)
Heat of combustion (C_v)	468.9 kcal./mole	(103)
Molar conductivity (0.001 *M* solution in ammonia at −33°C.)	0.8	(160)
Heat of neutralization	6.78 kcal./mole	(103)
Entropy at 15°C.	35.63 cal./degree	(166)
Magnetic susceptibility (molal)	-61.74×10^{-6} e.m.u.	(142)
Density, d_4^{20}	1.571	(94)

of the ultraviolet spectrum indicates that melamine is in the amide form in neutral solution. Addition of acid or base causes modification in the structure.



The structure of melamine has been studied recently (47) by a theoretical approach, by calculating the electronic transitions and ground-state energies of the two structures. The spectrum can be accounted for satisfactorily by the triamide structure but not by the isomelamine structure.

The infrared absorption spectra at 2–15 μ of melamine and its hydrochloride have been determined (156), but no useful correlations to structure were found.

The x-ray crystal structure of melamine has been examined by several investigators (76, 159); the dimensions of the unit cell are, in Ångström units:

	δ	π
a =	10.54	10.52
b =	7.54	7.44
c =	7.75	7.33

There are four molecules per unit cell. The positions of the atoms correspond to a resonance hybrid.

B. General chemical properties of melamine

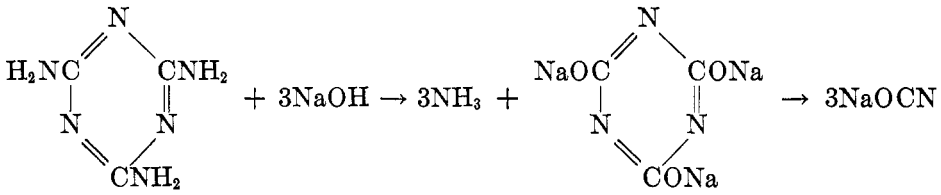
The amino groups confer basic properties on melamine, which gives readily hydrolyzable crystalline salts. Its pK_b is 9.0 (49), a value which means that it is a slightly stronger base than aniline ($pK_b = 9.5$).

The analysis of aqueous solutions of melamine can be carried out by titrating between pH 7.0 (phenolphthalein end point) and pH 3.35 (bromothymol blue) (30).

In contrast to aliphatic and aromatic amines melamine does not react with alkyl halides to give alkyl derivatives, and it reacts only slowly with acid chlorides. Ostrogovich (137) could not obtain any benzoyl derivative by using the Schotten–Baumann reaction or by fusion with benzamide. Acid anhydrides react, but excess of reagent and prolonged boiling are required. Melamine reacts slowly with sodium hypobromite, nitrogen being evolved (41).

Boiling with aqueous alkali brings about stepwise hydrolysis to the corresponding hydroxydiaminotriazine (ammeline), the dihydroxyaminotriazine (ammelide), and finally the trihydroxytriazine (cyanuric acid).

Hydrolysis to ammeline also occurs on boiling with concentrated nitric acid or heating with concentrated sulfuric acid to 150°C. Boiling with dilute nitric acid gives cyanuric acid. Oxidation with potassium permanganate also gives cyanuric acid (180). Destruction of the triazine ring only occurs under severe reaction conditions such as heating to 500°C. with alkali or alkali carbonates. In this case the product is an alkali cyanate (25, 104, 180). The reaction may be regarded as hydrolysis followed by depolymerization:



With metallic potassium, or with potassium hydroxide when an excess of melamine is used, polymerization occurs, and the product obtained is the potassium salt of melon, ammonia being evolved.

Rupture of the ring also takes place on heating with ammonium thiocyanate to 250–350°C., guanidine thiocyanate being obtained (167).

Other properties based on the action of reagents to give substituents on the exocyclic nitrogen atoms or on the ring nitrogen atoms (isomelamine structure) are discussed in the various sections below.

III. MELAMINE SALTS

A large number of melamine salts have been described in the literature (see table 3). With certain exceptions the simpler salts crystallize well and have a solubility in water similar to that of melamine itself.

In liquid ammonia melamine can form salts with alkali metal amides; the salts $KC_3H_3N_6 \cdot NH_3$ and $K_3C_3H_3N_6$ have been reported (62, 63).

TABLE 3

Melamine salts

Salt	Composition	Solubility in Water	Solubility in Alcohol	References
		g./100 ml.		
Hydrochloride	$C_3H_6N_6 \cdot HCl \cdot 1.5H_2O$	Soluble	Insoluble	(107)
Trihydrochloride	$C_3H_6N_6 \cdot 3HCl$	—	—	(26)
Hydrobromide	$C_3H_6N_6 \cdot HBr$	Soluble	Soluble	(38)
Hydroiodide	$C_3H_6N_6 \cdot HI$		Soluble	(38)
Thiocyanate	$C_3H_6N_6 \cdot HSCN$	Soluble in hot water; slightly soluble in cold water	Soluble	(39, 143)
Nitrate	$C_3H_6N_6 \cdot HNO_3$	0.68 (29°C.)	—	(15, 144)
Phosphate	$C_3H_6N_6 \cdot H_3PO_4 \cdot H_2O$	0.43 (29°C.)	—	(180)
Sulfate	$(C_3N_6H_6)_2 \cdot H_2SO_4 \cdot 2H_2O$	0.197 (29°C.)	Insoluble	(23, 79)
Picrate	$C_3H_6N_6 \cdot C_6H_2(OH)(NO_2)_3$	Very slight	—	(96)
Chloroplatinate	$(C_3H_6N_6)_2 \cdot H_2PtCl_6 \cdot 2H_2O$	Very slight	Insoluble	(74)
Monoöxalate	$C_3H_6N_6 \cdot H_2C_2O_4$	Very slight	Insoluble	(137)
Dioxalate	$(C_3H_6N_6)_2 \cdot H_2C_2O_4$	Very slight	Insoluble	(106, 137)
Phosphotungstate	—	Very slight	Insoluble	(171)
Metaphosphate	$C_3H_6N_6 \cdot HPO_3$	Very slight	—	(174)
Pyrophosphate	$(C_3H_6N_6)_4 \cdot H_4P_2O_7$	Very slight	—	(175)

TABLE 4

Solubility of melamine sulfate and nitrate in water

Temperature, °C.	0	22	23.5	40	60	80	92	95
Sulfate, g./100 ml.	0.12	0.16		0.30	0.51	0.95		1.50
Nitrate, g./100 ml.	ca. 0.2		0.456	0.85	0.20	0.50	0.785	

With silver nitrate the double salts $C_3N_6N_6 \cdot AgNO_3$ and $C_3H_6N_6 \cdot 2AgNO_3$ are formed.

The picrate melts at 316–317°C.

The solubilities of the sulfate and nitrate in water have been determined at various temperatures (68) (see table 4).

Salts of melamine and organic acids are listed in table 5.

The melamine salt of penicillin is prepared from melamine hydrochloride and sodium penicillin (35). In an example, melamine hydrochloride was prepared by boiling 25 g. of melamine with 400 ml. of 6 *N* hydrochloric acid until all was dissolved. Sodium penicillin G (3 g.) was dissolved in the minimum amount of water and mixed with 1.44 g. of melamine hydrochloride in 40 g. of water. A precipitate appeared at once. Sodium chloride (5 g.) was added to assist precipitation, and the product was dried over phosphorus pentoxide.

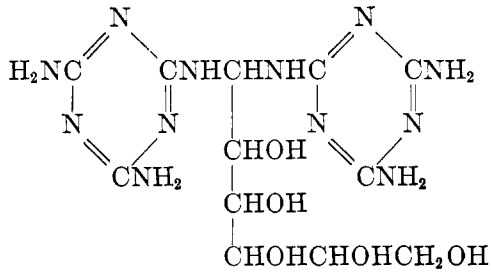
IV. MELAMINE COMPLEXES

A. Melamine-phosphorus pentoxide

When melamine and phosphorus pentoxide in the ratio of 2–4 moles of melamine to 1 mole of phosphorus pentoxide are heated to 400°C., an insoluble complex is obtained (115). The product is used in flameproofing (see page 167).

B. Melamine-glucose

Radelburgher (148) prepared a complex of melamine and glucose by refluxing equimolecular proportions of the two substances in aqueous alcohol (100 ml. of water and 50 ml. of ethanol) for 5 hr. The product melted at 218°C. after recrystallization from aqueous alcohol and was believed to have the following structure:



V. ALKYL- AND ARYLMELAMINES; ALKYL- AND ARYLISOMELAMINES

A. From melamine and amine hydrochlorides

If melamine is heated with amine hydrochlorides at 180–200°C. for some hours (77, 182), alkylmelamines are formed; e.g., 63 parts of melamine and 67 parts of methylamine hydrochloride (i.e., a molar ratio of 1:2) gave 50–55 parts of N^2,N^4-dimethylmelamine, m.p. 260–261°C., together with small amounts of unchanged melamine and N^2,N^4,N^6-trimethylmelamine, m.p. 130°C.

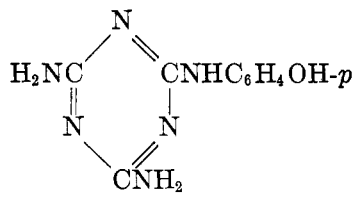
Similarly, melamine and aniline hydrochloride (3 moles) gave N^2,N^4,N^6-triphenylmelamine, m.p. 225°C. When, however, melamine hydrochloride was caused to react with aniline, the product obtained was 1,3,5-triphenylisomelamine, m.p. 185°C.

Dimethylamine hydrochloride (2 moles) and melamine (3 moles) give N^2,N^2-dimethylmelamine, m. p. 307–308°C. Octadecylamine hydrochloride (2 moles) and melamine (1 mole) react to give N^2,N^4-dioctadecylmelamine, m.p. 225°C.

B. From melamine and amines

The free amines react with melamine to give alkyl- or arylmelamines if higher temperatures are used (usually 350–500°C.). A patent (11) claims the formation of large numbers of such compounds, including aralkyl- and cycloalkylmelamines. Mono-*N*-substituted melamines are obtained by using small proportions of the amine in the reaction.

In a similar way hydroxyarylaminomelamines are obtained by heating melamine with aminophenols in an inert solvent at 150°C. (31, 43). Suitable solvents are ethylene glycol and propylene glycol; e.g., heating 109 g. of *p*-aminophenol and 126 g. of melamine in 800 g. of ethylene glycol for 8½ hr. at 160°C., then for 18 hr. at 180–190°C. and for 9 hr. at 190–200°C., produced *p*-hydroxy-N^2-phenylmelamine.



p-Hydroxy-N^2-phenylmelamine

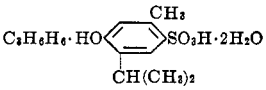
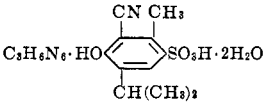
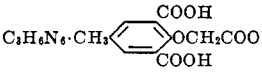
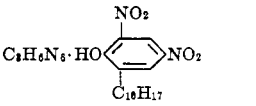
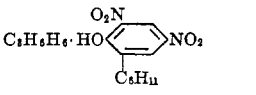
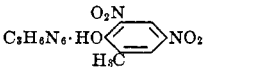
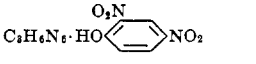
By using higher molar ratios of aminophenol to melamine it is possible to prepare di- and triphenylolmelamines. Aminocresols or naphthols may also be used.

C. Isomelamines

Melamine reacts with dialkyl sulfates to give monoalkylisomelamines. According to one patent (130), melamine is heated with dimethyl or diethyl

TABLE 5

Salts of melamine with organic acids

Salt	Formula	Reference
Chloroacetate	$C_3H_6N_6 \cdot CH_2ClCOOH$	(152)
Dichloroacetate	$C_3H_6N_6 \cdot CHCl_2COOH \cdot H_2O$	(152)
2-Naphthalenesulfonate	$C_3H_6N_6 \cdot C_{10}H_7SO_3H$	(152)
1-Naphthalenesulfonate	$C_3H_6N_6 \cdot C_{10}H_7SO_3H \cdot H_2O$	(152)
Sulfanilate	$C_3H_6N_6 \cdot NH_2C_6H_4SO_3H \cdot H_2O$	(152)
p-Toluenesulfonate	$C_3H_6N_6 \cdot CH_3C_6H_4SO_3H \cdot H_2O$	(152)
p-Thymolsulfonate		(152)
o-Cyano-*p*-thymolsulfonate		(152)
2-Carboxymethoxy-5-methylisophthalate		(152)
Orange II	$C_3H_6N_6 \cdot SO_3HC_6H_4N{=}NC_{10}H_6OH$ (yellow crystals)	(147)
Ponceau 6R	$(C_3H_6N_6)_2 \cdot C_{10}H_7N{=}NC_{10}H_4(OH)(SO_3H)_2$ (red)	(147)
Dinitrobornylphenol		(147)
Dinitro-*o*-cyclohexylphenol		(121)
Dinitro-*o*-cresol		(121)
Dinitrophenol		(121)

sulfate, and the dry mixture is slurried with water and then neutralized with caustic soda to liberate the respective free bases: methylisomelamine hydrate, obtained as crystals melting at 259–260°C. with decomposition, and ethylisomelamine, melting at 270°C. with decomposition.

According to a recent patent (82) the method was improved by carrying out the reaction in an ether solvent. Equimolecular quantities of dimethyl sulfate and melamine were slurried in 500 ml. of dioxane and then heated under reflux for 4 hr. to give the methylisomelamine salt of methyl hydrogen sulfate. The product was washed with 350 ml. of benzene and dried in air to give a 99 per cent yield of the pure salt. Suspension of the salt in water and addition of 20 per cent sodium hydroxide solution gave methylisomelamine monohydrate. Anhydrous methylisomelamine, obtained by drying the monohydrate *in vacuo*, melted at 238°C. with decomposition.

D. Isomerization of isomelamines

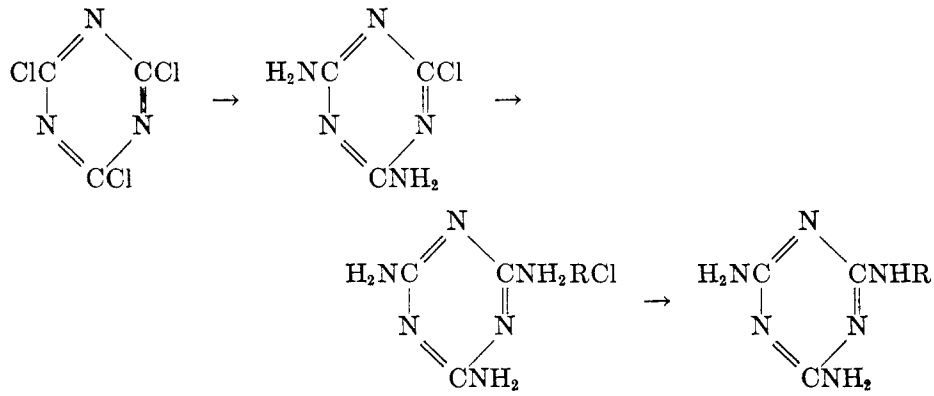
Isomelamines are isomerized to melamines by heating with an alcohol and a strongly basic substance (14). Thus butylmelamine, m.p. 160–162°C., was obtained by heating 5 g. of butylisomelamine with 0.3 g. of sodium in 100 ml. of 1-butanol for 3 hr. at reflux temperature. Similar results were obtained with dodecylisomelamine, 2-hydroxyethylisomelamine, and phenylisomelamine.

Rathke (149) isomerized triphenylisomelamine to triphenylmelamine by heating it with hydrochloric acid to 100–150°C. or with alcohol and ammonia to 150°C.

E. From cyanuric chloride

Several alkylated and arylated melamine derivatives have been prepared from cyanuric chloride.

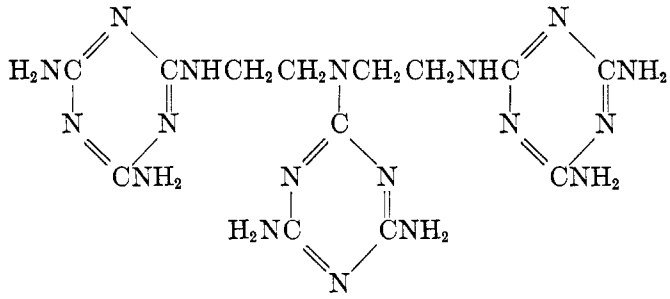
Cyanuric trichloride is heated with ammonia in a nonhydroxylic solvent at 60–90°C. to give chlorodiaminotriazine, and this is treated with amines at 80–100°C. in water (91). Caustic soda is then added to liberate the free base from the hydrochloride formed.



With aniline, an 85–90 per cent yield of phenylmelamine, m.p. 205°C., was obtained.

Similarly, with secondary amines N^2,N^2-disubstituted melamines have been prepared.

Diethylenetriamine gives diethylenetrimelamine (52), m.p. 314–316°C.



Diethylenetrimelamine

Other compounds prepared from chlorodiaminotriazine are listed in table 6. A number of N^2,N^4-substituted melamines were prepared from aminodichlorotriazine (see table 7). Similarly, N^2,N^4,N^6-substituted melamines were prepared from 2-chloro-4,6-dialkyl(or aryl)amino-*s*-triazines and primary or secondary amines (see table 8).

Triethylenemelamine has been prepared from ethylenimine and cyanuric chloride in benzene, using triethylamine as a base (69).

TABLE 6

N^2,N^2-Substituted melamines, $C_3H_4N_6RR'$ (*91*)

R	R′	Yield	Crystals from	Melting Point
		per cent		°C.
Ethyl	H	96	Aqueous ethanol	171–172
Butyl	H	90	2-Propanol	167–169
Phenyl	H	96	Methanol	204–205 (d.)
o-Phenylphenyl	H	98	Acetic acid	191–193
p-Sulfophenyl	H	95	Water	Infusible
Ethyl	Ethyl	93	2-Propanol	168–170
Ethylene (bis)	H	90	Water	314–316
Ethylene (bis)	Cyclohexyl	91	Aqueous cellosolve	338–340

TABLE 7

N^2,N^2,N^4,N^4-Substituted melamines, $C_3H_2N_6(RR')_2$ (*91*)

R	R′	Yield	Crystals from	Melting Point
		per cent		°C.
Ethyl	H	91	Aqueous ethanol	156–158
Cyanomethyl	H	80	Water	200
2-Hydroxyethyl	H	86	Methanol	160–161
3-Hydroxypropyl	H	—	Methanol	110–112
Phenyl	H	96	2-Propanol	219–220
p-Ethoxyphenyl	H	87		(Hydrochloride)
Phenyl	Methyl	98	2-Propanol	166–167
Ethyl	Ethyl	97	Aqueous methanol	71–72
2-Hydroxyethyl	2-Hydroxyethyl	100	Methanol	128–129
Oxydiethylene, —$CH_2CH_2OCH_2CH_2$—		100	Aqueous ethanol	170–172

TABLE 8

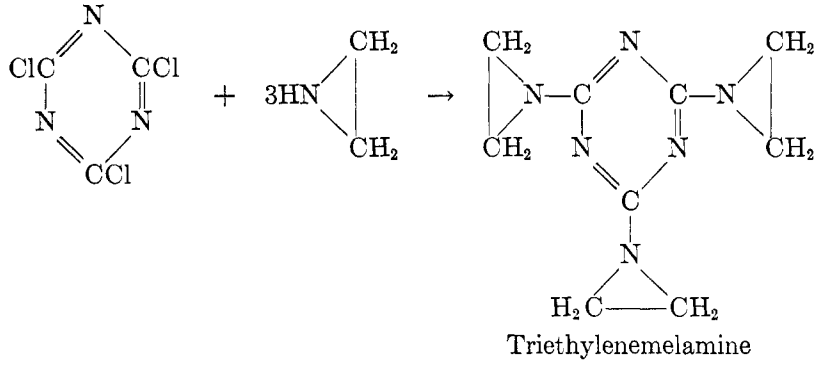
N^2,N^4,N^6-Substituted melamines (91)

Derivative of Melamine	Yield	Crystals from	Melting or Boiling Point
	per cent		°C.
N^2,N^4,N^6-Triethyl-	91	Aqueous ethanol	72–75
N^2,N^4,N^6-Tri(2′-hydroxyethyl)-	100	1-Butanol	100–101
N^2,N^4,N^6-Tri(3′-hydroxypropyl)-	87	Ethyl acetate	113–114
N^2,N^4-Di(2′-hydroxyethyl)-N^6-phenyl-	94	Methanol	134–135
N^2,N^4-Di(2′-cyanoethyl)-N^4,N^6-diphenyl-	84	Aqueous acetone	181–183
N^2,N^2,N^4,N^4,N^6,N^6-Hexa(2′-hydroxyethyl)-	65	1-Butanol	169–170
N^2,N^4,N^6-Tricyanomethyl-N^2,N^4,N^6-tricyclohexyl-	82	Methanol	165–167
N^2,N^4,N^6-Tricarboxymethyl-N^2,N^4,N^6-tricyclohexyl-	91	Methanol	136–137
N^2,N^4,N^6-Tricyanomethyl-N^2,N^4,N^6-tridodecyl-	67	Methanol	46–48
N^2,N^4,N^6-Triphenyl-*	—	Methyl cellosolve	232–234
Pentaethyl-†	95		120–121/0.4 mm. (b.p.)
Hexaethyl-	93		46–47
			151–154/2–3 mm. (b.p.)
Hexamethyl-‡	37	Methanol	172–174

* N^2,N^4,N^6-Triphenylmelamine was obtained by direct fusion of cyanuric chloride with 3 moles of aniline at about 300°C.

† Pentaethylmelamine was prepared by the reaction of 2-chloro-4,6-bis(diethylamino)-s-triazine with 2-4 moles of 70 per cent ethylamine at 110°C. under pressure in dioxane solution.

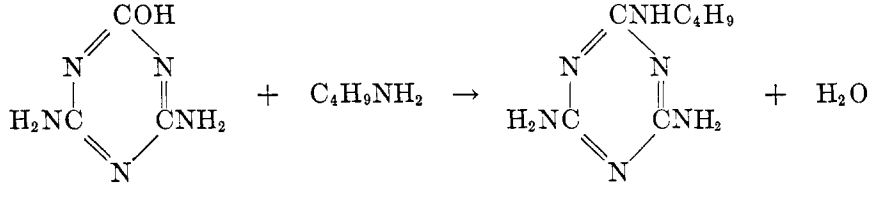
‡ Hexamethylmelamine was prepared from cyanuric chloride and 26 per cent aqueous dimethylamine in boiling acetone.



Triethylenemelamine

F. From hydroxytriazines

Ammeline, ammelide, or cyanuric acid is converted into melamine derivatives (113) if heated with a primary or secondary alkyl- or arylamine in a closed reaction vessel at a minimum temperature of 300°C. Thus, a mixture of 42 g. of ammeline and 25 g. of butylamine when heated at 350°C. for 2 hr. gave 7.6 g. of N^2-butylmelamine and small amounts of N^2,N^4-dibutylmelamine.



N^2-Butylmelamine

With 43 g. of ammeline and 50 g. of butylamine under the same conditions, the product was a mixture of mono-, di-, and tributylmelamines.

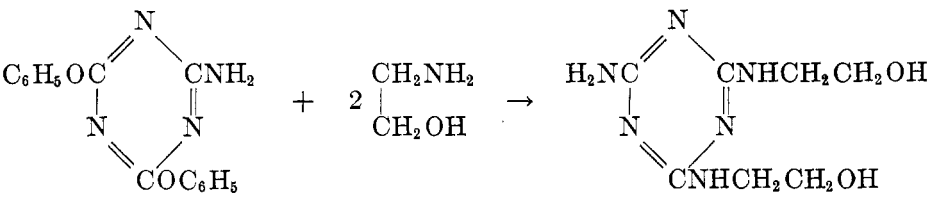
Heating a mixture of 42 g. of ammeline and 31 g. of aniline at 350°C. for 2 hr. gave 24.1 g. of phenylmelamines, of which monophenylmelamine was the major constituent.

G. Melam, melem, and melon

These polymers of melamine can be converted into melamine by heating with ammonia at 350°C. If a primary or secondary amine is used instead of ammonia, substituted melamines are obtained (110). For example, 47 parts of melam was heated with 37 parts of butylamine at 450°C. for 1 hr. to give 9.5 parts of mixed *n*-butylmelamines.

H. From triazinyl ethers

Substituted melamines may be prepared by the condensation of aryloxy-*s*-triazines with amines, and this is the best method of preparation for some of these derivatives (173). Thus, 2-amino-4,6-bisphenoxy-*s*-triazine (1 mole) and monoethanolamine (3 moles) heated for 3 hr. at reflux (180°C.) gave a 93.5 per cent yield of N^2,N^4-bis(2′-hydroxyethyl)melamine, m.p. 160–162°C.



N^2,N^4-Bis(2′-hydroxyethyl)melamine

In a similar way, tris(2′-hydroxyethyl)melamine was obtained from triphenyl cyanurate.

I. From thioammeline

Thioammeline, which can be prepared from dicyandiamide, reacts with amines when heated to 180°C. to give substituted melamines. Thus, heating 0.25 mole of thioammeline with 1.0 mole of aniline to 180°C. for 55 hr. resulted in evolution of hydrogen sulfide and the formation of a mixture of monophenyl- and triphenylmelamines (44); pure phenylmelamine, m.p. 225°C., and N^2,N^4,N^6-triphenylmelamine, m.p. 212–215°C., were isolated. Melamine itself did not react with aniline under these conditions of temperature and pressure.

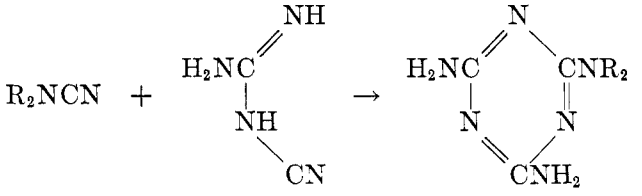
J. From dicyandiamide

Alkyl- and arylmelamines have been prepared (92) by heating dicyandiamide and amines together. For example, when 300 parts of dicyandiamide and 90 parts of diethylamine were heated to 120°C., a violent exothermic reaction set in and the temperature rose to 220°C. On cooling there was obtained 320 parts of crude product, which was worked up by extraction with ethanol or 1-butanol.

Melamine remained undissolved, but N^2,N^2-dimethylmelamine, m.p. 307–308°C., crystallized out when the solution was cooled. On partial evaporation of the mother liquor N^2,N^2,N^4,N^4-tetramethylmelamine was obtained, m.p. 220–222°C. An alternative method of purification is dissolution in dilute formic acid and neutralization of the acid with ammonia in steps; N^2,N^2-dimethylmelamine precipitates first. Butylamine reacts in a similar way to give butylmelamine, m.p. 180–185°C. (from benzene), and N^2,N^4-dibutylmelamine, which is isolated as the hydrochloride, melting at 45–47°C. Isobutylamine when heated with dicyandiamide in xylene suspension gave a mixture of monoisobutylmelamine, m.p. 160–166°C., and diisobutylmelamine monohydrochloride, m.p. 230–235°C. When a mixture of 120 parts of dicyandiamide and 290 parts of aniline was heated in an autoclave at 140–145°C. for 10–12 hr. at 20 atm. pressure and the product was cooled and extracted with alcohol, 53 parts of mixed phenylmelamines was obtained.

Monosubstituted melamines can be made from monosubstituted cyanamides if the alkyl group is tertiary. By refluxing solutions of dicyandiamide in 1-butanol or 1-propanol with powdered potassium hydroxide and *tert*-octylcyanamide, a 68 per cent yield of *tert*-octylmelamine was produced. *tert*-Butylcyanamide gave an 82 per cent yield of *tert*-butylmelamine, and 1-methylcyclohexylcyanamide gave a 72 per cent yield of the substituted melamine (29a).

N^2,N^2-Disubstituted melamines are obtained by the reaction of disubstituted cyanamides with dicyandiamide in a water-miscible solvent in the presence of an alkali catalyst (10, 81). The reaction is identical with the one used to prepare guanamines from substituted nitriles (24).



Dicyandiamide

Thus, the reaction when 70 parts of dimethylcyanamide and 101 parts of dicyandiamide were heated in 250 parts of 1-butanol at 90°C. in the presence of 6.6 parts of 85 per cent potassium hydroxide gave, after the reaction mixture was cooled in ice, an 81.5 per cent yield of N^2,N^2-dimethylmelamine, m.p. 307–308°C. with decomposition. The following compounds were prepared similarly: N^2,N^2-diethylmelamine, m.p. 177–178°C., in 74 per cent yield; N^2,N^2-diallylmelamine, m.p. 144–145°C., in 75 per cent yield; N^2,N^2-dibenzylmelamine, m.p. 222–223°C., in 67 per cent yield. Methyl, ethyl, or butyl cellosolves are also possible solvents (10).

A procedure (80) for preparing guanamines from dicyandiamide and nitriles in liquid ammonia can be extended to the preparation of dialkylmelamines. The reaction of diallylcyanamide with dicyandiamide in liquid ammonia gave diallylmelamine in nearly theoretical yield (30).

K. From dicyanoguanidine

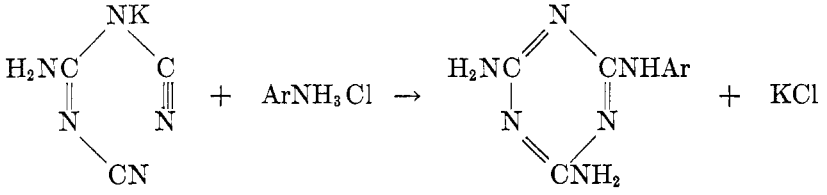
The reaction of dicyandiamide with cyanogen chloride in acetone in the presence of potassium hydroxide yields dicyanoguanidine (88). This product

$$NH{=}C(NH_2)NHCN + CNCl + 2KOH \rightarrow CNN{=}C(NH_2)NKCN + KCl + 2H_2O$$

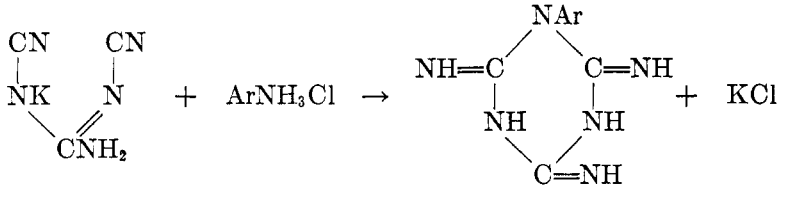
Dicyanoguanidine

reacts with aliphatic and aromatic amines to give either normal or isomelamine derivatives (12).

At a pH below 1, arylamines yield arylmelamines: e.g., 18.6 g. of aniline in 51 ml. of concentrated hydrochloric acid and 24 ml. of water was heated at 98°C. with 32 g. of potassium dicyanoguanidine in 75 ml. of water for 20 min. Phenylmelamine, m.p. 204°C., was obtained in 62 per cent yield. *p*-Phenylenediamine under similar conditions gave *p*-phenylenebismelamine.

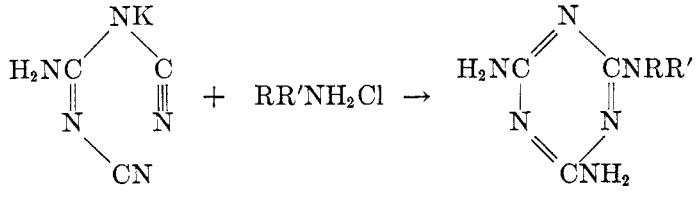


At a pH above 1, preferably about 3, isomelamines are formed (3, 84). Aniline in dilute hydrochloric acid reacted with potassium dicyanoguanidine at 92°C. to give phenylisomelamine hydrochloride, m.p. 318°C. The free base, which was liberated by treatment of the salt with alkali, melted at 232°C. A large number of isomelamine derivatives are described in these patents.



These compounds are all strong bases.

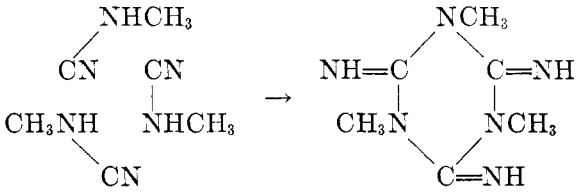
Secondary amine salts form N^2,N^2-disubstituted melamines (129).



Thus, when equimolar proportions of diethylamine hydrochloride and potassium dicyanoguanidine were heated to 145°C. an exothermic reaction took place and the temperature rose to 190°C. The product was dissolved in dilute hydrochloric acid, filtered, and reprecipitated to give N^2,N^2-diethylmelamine.

L. From cyanamide

Symmetrical alkyl- or arylisomelamines are obtained by the trimerization of monoalkylcyanamides. On alkylating cyanamide with dimethyl sulfate (48) in the presence of alkali, both mono- and dimethylcyanamides were formed. On extraction with ether, dimethylcyanamide was removed, and the aqueous layer deposited 1,3,5-trimethylisomelamine as a trihydrate, m.p. 123–124°C. The anhydrous material melts at 179°C.

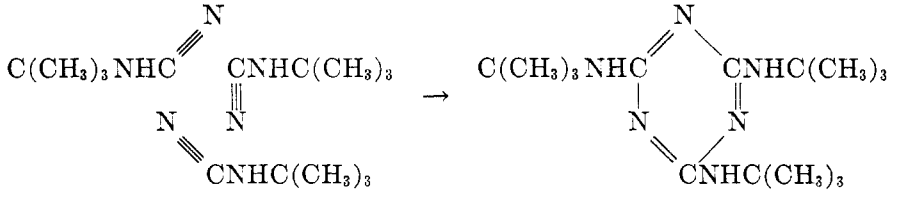


1,3,5-Trimethylisomelamine

An aqueous solution of trimethylisomelamine has a strongly alkaline reaction.

Triethyl-, triisoamyl-, triphenyl-, tri-*p*-tolyl-, and tribenzylisomelamines are formed in a similar way from the corresponding cyanamides (17, 27, 67, 72, 170).

According to a recent patent (83) *tert*-alkylcyanamides yield trisubstituted *normal* melamines by polymerization in an inert solvent in the presence of strong alkali. Thus, *tert*-butylcyanamide on being heated with 8 parts of 50 per cent aqueous methanol under reflux for 24 hr., using a pellet of potassium hydroxide as catalyst, gave tri-*tert*-butylmelamine, m.p. 175–180°C.



Tri-*tert*-butylmelamine

Tri-*tert*-octylmelamine was also described.

M. From urea

Substituted melamines are prepared (111) by heating urea or an alkyl- or arylurea with a primary or secondary alkyl- or arylamine in a closed reaction vessel at 300°C. (minimum temperature): e.g., 60 g. of urea when heated with 25 g. of butylamine in a 300-ml. autoclave at 400°C. for 2 hr. gave a product containing 4.7 g. of melamine, 12.9 g. of butylmelamine, and 1.0 g. of N^2,N^4-dibutylmelamine. The reaction of butylmelamine, aniline, and urea at 350°C. for 2 hr. gave a mixture of N^2,N^2,N^4- and N^2,N^4,N^6-triphenylmelamines.

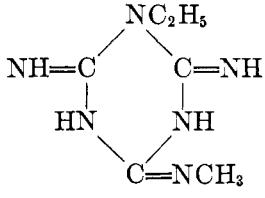
N. From carbon monoxide and ammonia

A 300-ml. autoclave was charged with 15 g. of catalyst (50 per cent nickel on silicon dioxide), 35 g. of methylamine, 15 g. of ammonia, and 12 g. of carbon

monoxide (6). After the mixture had been heated to 335°C. for 5 hr., a product consisting of a mixture of mono-, di-, and trimethylmelamines was obtained.

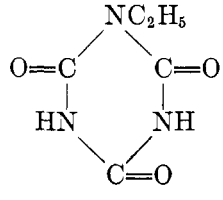
O. Structures

Proof of the structure of these derivatives is provided by hydrolysis with dilute hydrochloric acid, which results in removal of the substituted amino groups but not the ring-substituted nitrogen atoms. Thus, substituted melamines all give cyanuric acid on hydrolysis, but ring-substituted isomelamines give substituted isocyanuric acids, and isomelamines with both amino and ring nitrogen substituents give substituted isocyanuric acids containing a lower number of substituents (63, 73); for example:



+ 3HCl + $3H_2O$ →

1-Ethyl-N^4-methyl-isomelamine

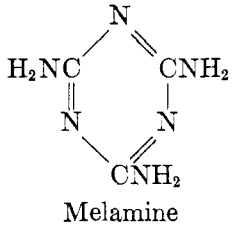


+ $2NH_4Cl$ + CH_3NH_3Cl

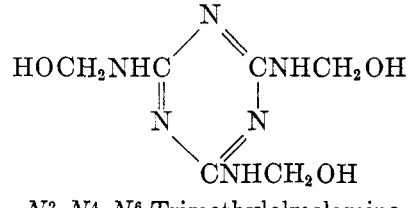
Ethylisocyanuric acid

VI. METHYLOLMELAMINES

The primary reaction products of melamine and formaldehyde are the methylolmelamines.



+ 3HCHO →



Melamine

N^2,N^4,N^6-Trimethylolmelamine

Numerous patent specifications describe conditions for the preparation of soluble materials having the approximate composition of mono-, tri-, or hexamethylolmelamines, but usually only in the form of a syrup which is then reacted further with excess formaldehyde to give polymers or is coverted into oil-soluble ethers by alkylation.

Conditions for the isolation of compounds of definite composition must be

very precise. Earlier publications (64, 71) describe only hydrated derivatives of methylolmelamine. Thus, Dixon, Woodberry, and Costa (49) heated melamine at 75°C. with 3.3 moles of 37–40 per cent formaldehyde (pH adjusted to 8.0 with sodium hydroxide). Complete solution was obtained in half an hour. The solution was cooled and poured on to shallow trays to "crystallize" the trimethylolmelamine as a solid cake, which was dried at 50°C. for 12 hr. The solid product was "essentially trimethylolmelamine, but contained a small fraction of polymerised product." Di- and hexamethylolmelamines were obtained by the same procedure, using different proportions of formaldehyde.

It is possible (30) to prepare both tri- and hexamethylolmelamines having the correct molecular compositions. The conditions of reaction need to be closely specified in regard to trimethylolmelamine. Melamine and formaldehyde (3.0 moles), neutralized to pH 8 with caustic soda, were heated to 67°C. for 13 min., by which time all the melamine had dissolved. The solution was poured on to a porcelain tray to "crystallize," and the solid was filtered off, washed, and dried in a desiccator. Hexamethylolmelamine was prepared by heating melamine with 8 moles of formaldehyde at 69°C. for 13–23 min. and working the product up in the same way as above.

Wohnsiedler (181) heated melamine with paraform (3 moles of CH_2O) at 60°C. for 20 min. at pH 10. Afterwards, glycine and sodium chloride were added as a buffer; after 1 day trimethylolmelamine separated as a thick granular paste, which was filtered off, washed, and dried in a desiccator.

Okano and Ogoto (134) studied the rates of condensation of melamine with formaldehyde at pH 3–10.6 at temperatures of 35°, 40°, and 70°C. In order to differentiate between free and combined formaldehyde, they employed both an iodimetric and a sulfite technique. The primary methylolmelamines consume iodine like formaldehyde itself but do not react with sulfite; condensed products no longer react with iodine.

The results show that the formation of methylol compounds occurs at 35–40°C., except in acid solution. The reaction is reversible throughout the pH range. The rate of irreversible condensation of methylolmelamine with melamine in neutral and acid media is very rapid at 70°C. Koeda (95) prepared methylolmelamine solutions and separated the mono to hexa derivatives by paper chromatography with butanol:ethanol:water (4:1:2) as solvent and Tollens reagent for coloration. Except in the reaction with 8 molar proportions of formalin (when the hexa derivative was the sole product), the other methylol products consisted of mixtures of the mono to hexa derivatives.

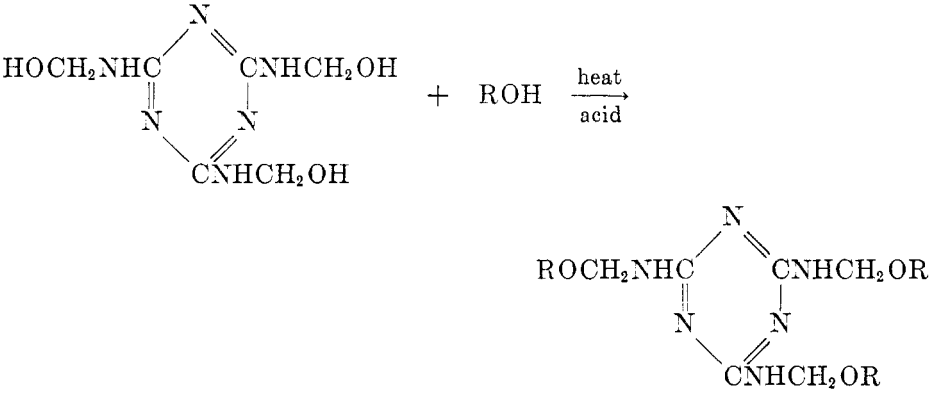
For the preparation of monomethylolmelamine, 37.5 g. of melamine was treated with 67 g. of 37 per cent aqueous formaldehyde and 14 g. of water at pH 9.0, and the temperature raised to 70°C. within 10 min. Paper chromatography revealed the immediate formation of monomethylolmelamine. Other methylolmelamines up to the hexa derivative were formed within 5 min. Raising the temperature over a period of 1 hr. instead of 10 min. gave similar results.

The reaction of melamine with formaldehyde cannot be generalized to apply to other aldehydes. Most aldehydes cannot be made to react with melamine,

and whereas resinous products have been described as having been made from furfural and melamine, compounds analogous to the methylolmelamines have not been identified. A compound of this nature, N^2,N^4-bis(2′,2′,2′-trichloroethylol)melamine has been prepared (20a) by dissolving melamine in an aqueous solution of chloral hydrate at 70–80°C. Solution occurred in 2 min. and then a granular solid separated out. Precipitation was complete in 5 min. The product had no melting point and evolved chloral on heating. It was hydrolyzed by boiling dilute sodium hydroxide to chloroform and melamine.

VII. METHYLOLMELAMINE ETHERS

Methylolmelamines are readily alkylated, by heating with alcohols in the presence of mineral acids, to give ethers.



Some of these compounds, e.g., the methyl, ethyl, and butyl ethers, find extensive use as intermediates for resin manufacture, but are usually only prepared in the form of solutions. There are a few descriptions of individual compounds.

For example, crystalline tris(methoxymethyl)melamine was prepared as follows (135): 126 parts of melamine was first dissolved in formaldehyde (486 parts of 37 per cent solution) at 60–70°C. with addition of caustic soda to maintain the pH at 7.5. The mixture was concentrated in a vacuum to 75 per cent solids, and then 844 parts of methanol was added, with sufficient phosphoric acid to neutralize the caustic soda. On distillation of the methanol, the trimethyl ether was obtained in a crystalline form.

Tris(ethoxymethyl)melamine, m.p. 134–138°C., has been described in two patents (53, 118). It was prepared from trimethylolmelamine by refluxing with ethanol in the presence of anhydrous hydrogen chloride.

VIII. ACYLMELAMINES

The acylation of melamine has been discussed by Ostrogovich (137). Acyl halides (e.g., benzoyl chloride in the Schotten–Baumann reaction) have no effect on melamine. The usual way to prepare acylmelamines is by prolonged heating with the acid anhydride or its amide.

A. Formylmelamine

Formylmelamine was obtained (137) by heating 1 part of melamine with 8 parts of formamide to 155°C. Treatment with 20 per cent acetic acid removed any unchanged melamine. The product was in the form of white scales, which on heating decomposed without melting.

B. Diacetylmelamine

Diacetylmelamine was obtained by Ostrogovich by heating 1 part of melamine with 35 parts of acetic anhydride under reflux for 2 min. The product was obtained as colorless needles melting at 305–306°C.

C. Triacetylmelamine

Triacetylmelamine was also prepared by Ostrogovich, using 200 parts of acetic anhydride to 1 part of melamine. The product melted at 298–300°C.

Cason (33) prepared triacetylmelamine by heating 30 g. of melamine with 5 g. of sodium acetate in an excess of acetic anhydride (450 ml.). The mixture became pasty owing to the formation of diacetylmelamine; upon prolonged boiling (6 hr. in all) soft shining plates of triacetylmelamine appeared. After filtration of the product, the excess acetic anhydride could be reused five more times for reaction with 30-g. portions of melamine.

D. Higher triacylmelamines

These acylmelamines have been extensively patented. The process is the same as for triacetylmelamine above, i.e., heating with the corresponding acid anhydride. The long-chain acid anhydrides are prepared by heating the corresponding fatty acids with acetic anhydride.

Melamine and the acid anhydride were stirred (55) in a flask heated in an oil bath. The temperature of the oil bath was raised to the desired value and maintained there for the period shown in table 9. The reaction mixture was cooled, diluted with methanol, ethanol, or ethyl acetate, and filtered. The product was recrystallized from glacial acetic acid.

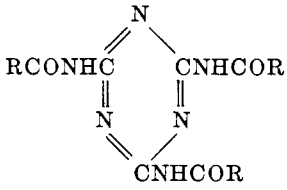
The triacylmelamines are unaffected by boiling water, but they are completely hydrolyzed to melamine by hot aqueous sodium hydroxide or sodium carbonate. When boiled with dilute hydrochloric acid, they are converted into a mixture of ammeline and ammelide.

The production of these compounds by the same procedure as described above has been patented by the Monsanto Chemical Company (56, 123).

Another patent covers the production of a similar compound derived from commercial tall oil (66). A mixture of 300 g. (approximately 1 mole) of tall oil (50 per cent resin acids, 40 per cent fatty acids) and 283 g. of acetic anhydride (3 moles) was heated for 4 hr under reflux, and the excess acetic anhydride was removed *in vacuo*. The resulting anhydride (120 g.) was heated with 4.2 g. of melamine at 195°C. for 1 hr.; on cooling, the trisubstituted melamine was obtained in 60 per cent yield as an amber-colored, semisolid mass, m.p. 197°C.

TABLE 9

Triacylmelamines from melamine and acid anhydrides (55)

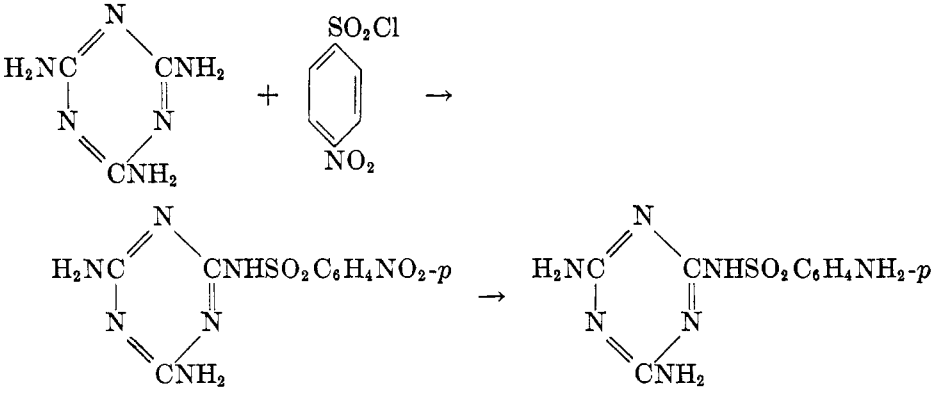


Anhydride	Moles of Anhydride	Temperature	Time	Yield	Melting Point of Triacylmelamine
		°C.	*min.*	*per cent*	°C.
Propionyl	8.1	158	15	94	282
Butyryl	12	160	30	98	258
Valeryl	10	172	30	94	228–229
Isovaleryl	12	167	15	85	216–218
Caproyl	8.8	175	15	91	220
Oenanthyl	10	160	5	90	210
Caprylyl	9.3	175	15	94	209
Pelargonyl	6.3	185	5	88	194–195
Lauryl	6.5	192	15	99	178–179
Stearyl	3.5	200	30	93	159–161
Oleyl	4.0	197	30	99	138–140
Benzoyl	8.3	172	60	84	201–203

IX. SULFONYLMELAMINES

A. From melamine

The melamine analog of the sulfa drugs, *p*-aminobenzenesulfonylmelamine, was obtained by the reaction of melamine with *p*-nitrobenzenesulfonyl chloride, followed by reduction (154). For example, 25 parts of melamine was heated and

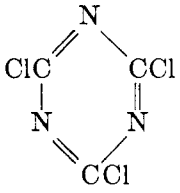


stirred with 30 parts of *p*-nitrobenzenesulfonyl chloride in 100 parts of pyridine at 60–70°C. When the mixture thickened, a further 100 parts of pyridine was added, and heating and stirring were continued for 30 min. The mixture was poured into 600 parts of water and filtered. The *p*-nitrobenzenesulfonylmelamine was purified by redissolution in sodium hydroxide solution and precipitation with

acid. Reduction of the nitro compound was achieved by heating with 2 parts of iron dust in 20 parts of 1 per cent acetic acid. The product, *p*-aminobenzenesulfonylmelamine, is a crystalline solid.

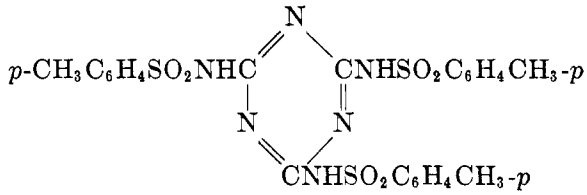
B. From cyanuric chloride

In contrast to the above reaction with *p*-nitrobenzenesulfonyl chloride in pyridine, Kurzer and Powell (101) found that tosyl chloride, i.e., *p*-toluenesulfonyl chloride, did not react with melamine under these conditions, nor was there any reaction with tosylamide in phenol or with tosyl anhydride on fusion. N^2,N^4,N^6-Tritosylmelamine was prepared by the reaction of cyanuric chloride with 6–7 moles of sodium tosylamide.



Cyanuric chloride

$$+\ 3p\text{-}CH_3C_6H_4SO_2NHNa \rightarrow$$



N^2, N^4, N^6-Tritosylmelamine

C. From sulfonylcyanoguanidines

Monosulfonylcyanoguanidines have been prepared from dicyandiamide by reaction with sulfonyl halides in alkaline media containing acetone as solvent (87, 89, 90).

$$RSO_2Cl + NH_2C(=NH)NHCN \rightarrow RSO_2NHC(=NH)NHCN$$

Kurzer and Powell (100) found that treatment of these latter compounds with a further quantity of sulfonyl chloride in pyridine yielded N^2,N^4,N^6-trisulfonylmelamines instead of the expected disulfonylcyanoguanidines (I). They postulated that these compounds were labile and decomposed immediately in pyridine solution with elimination of the elements of sulfonylcyanamide.

$$RSO_2NHC(=NH)NHCN \rightarrow RSO_2NHC(=NH)N(SO_2R)CN \rightarrow 2RSO_2NHCN$$

I

$$\Uparrow\Downarrow$$

$$RSO_2NHC(=NH)N{=}C{=}NSO_2R$$

II

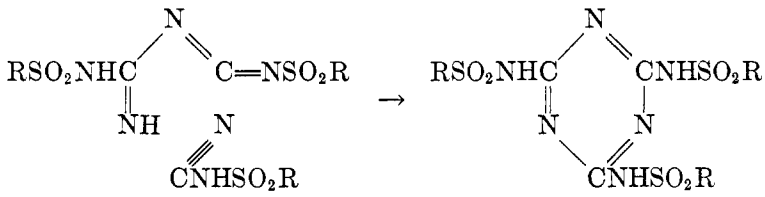
The sulfonylcyanamide formed would react with a further portion of the disulfonylcyanoguanidine in the tautomeric carbodiimide form (II) to yield an

TABLE 10

Trisulfonylmelamines (100)

Trisulfonylmelamine	Composition	Melting Point
		°C.
Trimethanesulfonylmelamine	$C_6H_{12}O_6N_6S_3 \cdot C_2H_5OH$	309–311
Tribenzenesulfonylmelamine	$C_{21}H_{18}O_6N_6S_3$	229–231
	$C_{21}H_{18}O_6N_6S_3 \cdot C_2H_5OH$	149–151
	$C_{21}H_{18}O_6N_6S_3 \cdot C_6H_6$	190–192
Tri-*o*-toluenesulfonylmelamine	$C_{24}H_{24}O_6N_6S_3$	294–295
Tri-*p*-toluenesulfonylmelamine	$C_{24}H_{24}O_6N_6S_3$	284–285
Tri-*p*-acetaminobenzenesulfonylmelamine	$C_{27}H_{27}O_9N_9NaS_3$	304–306
	$C_{27}H_{27}O_9N_9NaS_3 \cdot C_2H_5OH$	304–306

N^2,N^4,N^6-trisulfonylmelamine. Trisulfonylmelamines prepared in this way are listed in table 10.



The trisulfonylmelamines are tribasic acids, as shown by the formation of well-defined sodium and silver salts. They are soluble in aqueous alkali and reprecipitated by mineral acid. When freshly precipitated from aqueous alkali the products appear to be hydrated. These hydrated forms are highly soluble in boiling ethanol, methanol, or chloroform, from which they separate as crystalline products, frequently hydrated.

They are markedly stable against both acid and alkaline hydrolysis, but in concentrated sulfuric acid at 60–70°C. cleavage occurs to give melamine sulfate and the corresponding sulfonic acid.

X. DEPOLYMERIZATION OF MELAMINE

Melamine has been depolymerized to cyanamide (108). Melamine (9 g.) was heated in a quartz tube (24″ x 2½″) in an electric furnace in a stream of nitrogen. The melamine was vaporized at 360°C., and the vapor passed through a cracking zone at 635°C. The sublimate was collected, and on leaching with ether yielded pure cyanamide.

In an early patent (19) the depolymerization of melamine to disodium cyanamide was described, the melamine being melted with sodium amide and carbon at 350–600°C.

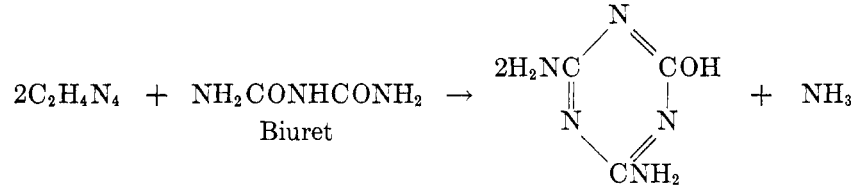
XI. HYDROLYSIS PRODUCTS OF MELAMINE

Stepwise hydrolysis of melamine to ammeline, ammelide, and cyanuric acid by the action of acids or alkalies has already been discussed (page 135). Combined

hydrolysis and depolymerization leading to the formation of sodium cyanate are achieved by heating with alkali carbonates (25, 104).

A. Ammeline, 4,6-diamino-2-hydroxy-1,3,5-triazine

Ammeline may also be prepared by the pyrolysis of urea (29) and by condensing 2 moles of dicyandiamide with 1 mole of biuret (21).



Ammeline

Ammeline is a white chalky powder having amphoteric properties and only trace solubility in water. Bann (30) gives the following data:

Temperature	Solubility	pK_a
°C.	*per cent*	
40	0.0074	9.65
90	0.048	8.9

Ammeline is so feebly acidic (162) that it can be dissolved in hot sodium carbonate solution to give a clear liquid, from which it crystallizes in the free state on cooling. It forms a crystalline nitrate, and the sulfate, chromate, and oxalate have been described (162, 180). The latter two salts have very little solubility in water. Naturally its basic properties are weaker than those of melamine.

Ammeline is soluble in aqueous alkalies and in mineral acids, but not in acetic acid.

Boiling ammeline with dilute hydrochloric acid gives melon and ammonia; boiling with dilute alkali gives ammelide.

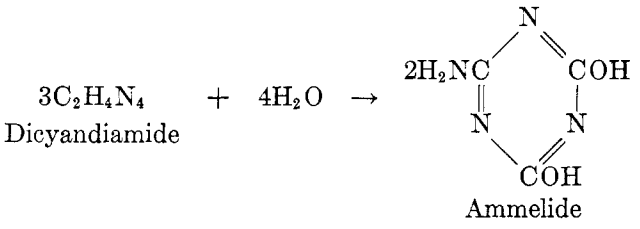
Ammeline does not melt, but decomposes at high temperatures. A characteristic derivative is the picrate, which forms orange needles, m.p. 266°C. (136).

Like melamine, ammeline shows little reaction with the usual reagents for the NH_2 and OH groups, and alkyl, acyl, etc. derivatives are usually prepared indirectly from cyanuric chloride.

The ammonolysis of ammeline to melamine has been described in several patents (112).

B. Ammelide, 6-amino-2,4-dihydroxy-1,3,5-triazine

Ammelide is obtained by heating melam (see page 155) with concentrated sulfuric acid for a short time at 190°C. (180) and pouring the product into a large excess of water, whereupon the sulfate slowly separates out. It is also obtained by heating dicyandiamide with aqueous ammonia (sp. gr. 0.90) at 160–170°C. (22).



The reaction of cyanamide or of dicyandiamide with carbon dioxide in the absence of ammonia at 10–14 atm. and at 60–200°C. in the presence of a solvent also gives ammelide, which is precipitated on cooling the reaction mixture (137).

$$C_2H_4N_4 + CO_2 \rightarrow C_3H_4N_4O_2$$

Ammelide

No method so far has been proposed for the isolation of ammelide from the "caustic solubles" sometimes present in crude melamine, since ammeline is present in a much greater proportion.

Ammelide is a white powder. It is insoluble in water and ordinary solvents but easily soluble in concentrated mineral acids, as well as in alkalies and ammonia.

Heated with water to 170°C., ammelide decomposes into carbon dioxide and ammonia. It is converted into cyanuric acid by potassium permanganate and other oxidizing agents, or by boiling with acids or alkalies.

When ammelide is heated in a stream of carbon dioxide it is converted into cyanamide (180).

$$C_3H_4N_4O_2 \rightarrow 2CH_2N_2 + CO_2$$

Ammelide Cyanamide

It is not attacked by chlorine, hydriodic acid, or acetyl chloride. With phosphorus pentachloride it yields cyanuric chloride.

Volhard and Striegler (177) have described the salts which ammelide forms with acids and bases (see table 11).

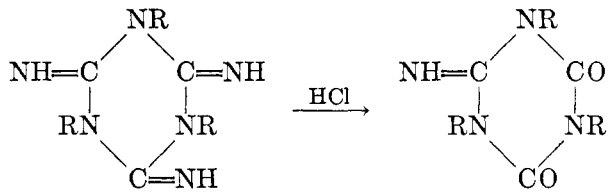
Alkylammelides have only been obtained indirectly; e.g., by the action of amines on cyanuric chloride or bromide.

Triethyl- and triphenylisoammelides are obtained by treating the corresponding trisubstituted isomelamine with hydrochloric acid.

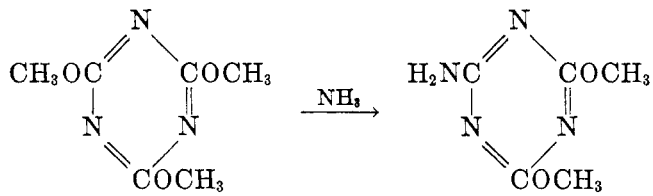
TABLE 11

Salts of ammelide

Salt Formed by Ammelide and	Formula of Salt	Salt Formed by Ammelide and	Formula of Salt
Nitric acid	$C_3H_3(NH_2)(OH)_2 \cdot 2HNO_3$	Calcium hydroxide	$C_3N_3(NH_2)(O_2Ca)$
Hydrochloric acid	$C_3N_3(NH_2)(OH)_2 \cdot 2HCl$	Barium hydroxide	$C_3N_3(NH_2)(O_2Ba) \cdot 2H_2O$
Sulfuric acid	$C_3N_3(NH_2)(OH)_2 \cdot H_2SO_4$	Nickel hydroxide	$C_3N_3(NH_2)(O_2Ni) \cdot 2H_2O$
Sodium hydroxide	$C_3N_3(NH_2)(ONa)_2 \cdot 6H_2O$	Silver hydroxide	$C_3N_3(NH_2)(OAg)_2$
Ammonium hydroxide	$C_3N_3(NH_2)(OH)(ONH_4) \cdot 1.5H_2O$	Silver hydroxide	$C_3N_3(NH_2)(OH)(OAg) \cdot 1.5H_2O$



Dimethylammelide is obtained by the action of ammonia on trimethyl cyanurate.



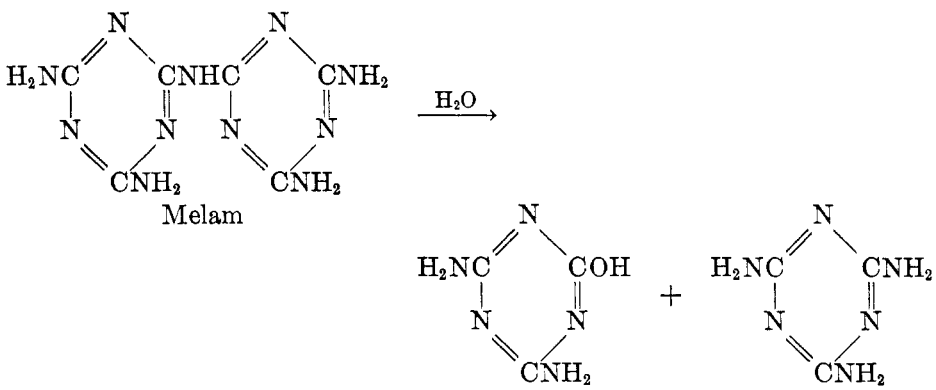
XII. CONDENSATION PRODUCTS OF MELAMINE

A. Melam, $C_6H_9N_{11}$

Melan was first discovered by Liebig (105), who obtained it from the residue left after heating ammonium thiocyanate. The residue contained melamine thiocyanate, melam thiocyanate, melem, and other products. It was washed with hot water, then with cold potassium hydroxide solution, and finally dissolved in dilute hydrochloric acid and then precipitated by neutralizing with potassium hydroxide.

Melam is a white powder which is insoluble in water and sparingly soluble in acids. On heating it loses ammonia to form first melem, and then the yellow compound melon.

According to Redeman and Lucas (151) melam has the constitution of a ditriazinylamine, and this is borne out by its hydrolysis with 30 per cent ammonia to form ammeline and melamine.



Melam

Ammeline Melamine

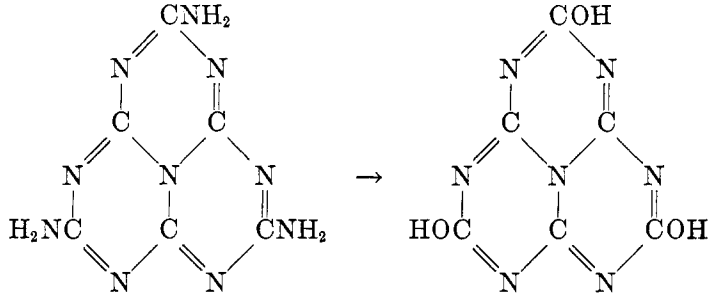
Treatment of melam with concentrated nitric acid yields cyanuric acid.

With ammonia under pressure melam is converted into melamine (109, 164).

B. Melem, $C_6H_6N_{10}$

Melem has been prepared by the pyrolysis of ammonium thiocyanate, when it is a by-product of melam production, or by further heating of melam or melamine. It may be separated from melam by boiling with a 5 per cent solution of potassium hydroxide for 24 hr.; melam is converted into ammeline, while the melem remains unchanged.

Melem is a white, water-insoluble powder, which when boiled with concentrated potassium hydroxide solution gives ammelide and ammonia. With potassium carbonate it yields the monopotassium salt of cyameluric acid (176). From the tricyclic structure assigned to the latter compound by Pauling (141), Redemann and Lucas (150) have suggested a related structure for melem.



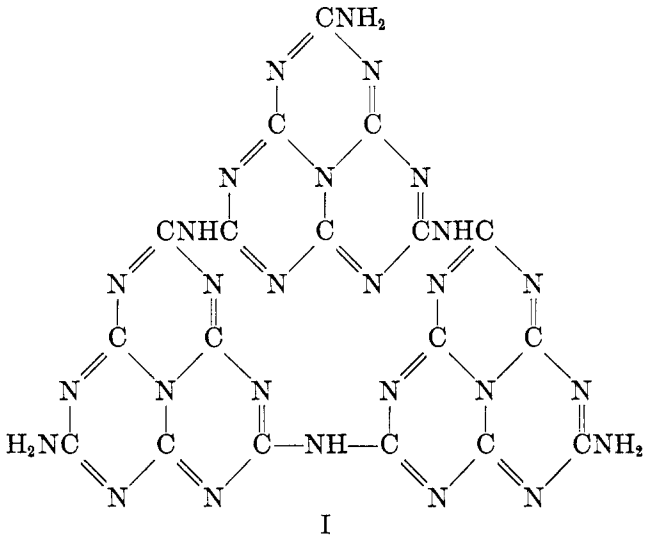
Melem Cyameluric acid

C. Melon, $(C_6H_3N_9)_x$

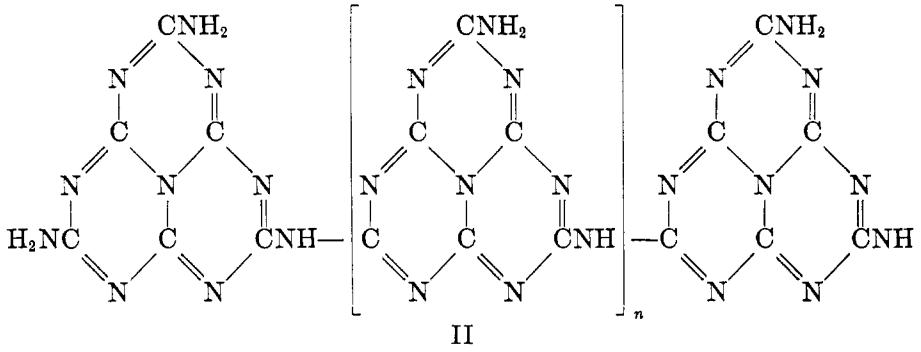
Melon is obtained by heating melamine, ammeline, ammelide, or ammonium thiocyanate to a dull red glow. The best method for the preparation of melon is described by Redemann and Lucas (150). Sodium thiocyanate is chlorinated at 70–80°C., and the sludge of "pseudothiocyanogen" is filtered off, washed, and dried at 120°C. On heating in a large porcelain basin until all volatile products are expelled, it is converted into melon. This is a light yellow powder, insoluble in water, dilute acids, or alkalies. Heated in nitrogen, it gives hydrogen cyanide and cyanogen. When heated in potassium hydroxide solution, it gives ammonia and the potassium salt of melam. Potassium melonate is obtained by adding melon to fused potassium thiocyanate and heating. On extraction with water it is obtained in fine felted needles (150). When boiled with 4 *N* potassium hydroxide melon gives potassium cyamelurate.

Franklin (62) found that the empirical composition of melon varied with the method of preparation, and obtained samples of hydrogen content varying from 1.1 to 2.0 per cent (theory for $C_6H_3N_9$ = 1.5 per cent).

Redemann and Lucas (151) have suggested that melon consists of planar cyameluryl rings joined through nitrogen atoms, as in the cyclic arrangement $C_{18}H_9N_{27}$ (I), or as a chain polymer (II) which approximates to the empirical composition $C_6H_3N_9$ if the chain is sufficiently long, i.e., n is large.



I

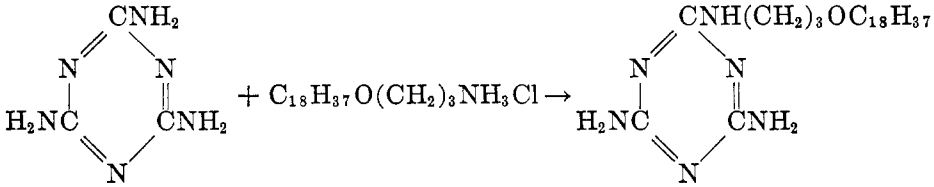


II

XIII. CONDENSATION OF MELAMINE WITH ALKYLENE OXIDES

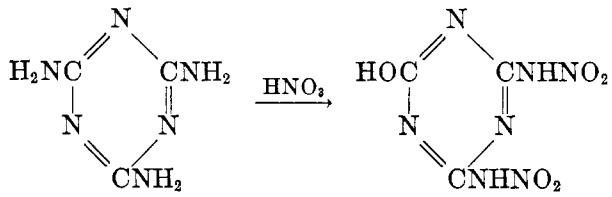
Melamine condenses with glycidol, CH_2CHCH_2OH (with an epoxide O bridging the two middle carbons), to form amber resins (57, 58). When 613 parts of melamine and 11.1 parts of glycidol were heated to 130°C., an exothermic reaction set in and the temperature rose to 220°C. The product was a nontransparent, soft resin, which was soluble in hot water. Upon being heated to 258°C. it became viscous and was then soluble in both hot and cold water. This reaction is also disclosed for melamine derivatives such as ammeline, guanidine, or alkylmelamines.

According to a second patent (58) the reaction of octadecyloxypropylamine hydrochloride with melamine at 200–210°C. yields octadecyloxypropylmelamine, which is then condensed further with glycidol.



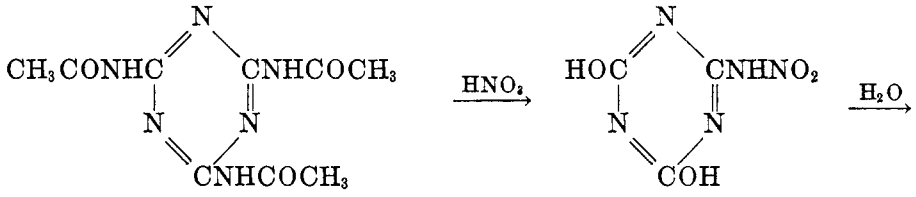
XIV. NITRATION OF MELAMINE

Cason (33) nitrated melamine and obtained a product of the empirical formula $C_3H_{3-4}N_7O_5$. The compound was identified by Atkinson (20) as N^2,N^4-dinitroammeline.

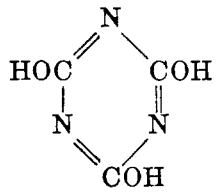


N^2,N^4-Dinitroammeline

Cason also nitrated triacetylmelamine to $C_9H_9O_{12}N_{15}$, which was identified by Atkinson as nitroammelide (actually $C_3H_3O_4N_5$), which is converted into cyanuric acid by heating with water.

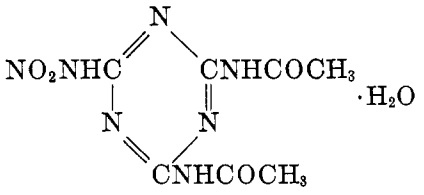


Triacetylmelamine Nitroammelide



Cyanuric acid

Atkinson also nitrated triacetylmelamine less vigorously and obtained N^2,N^4-diacetyl-N^6-nitromelamine in the form of its monohydrate.



Triacetylmelamine (10 g.) was dissolved in 40 ml. of fuming nitric acid (d = 1.50), and after 5 hr. at room temperature the solution was poured onto ice. A white solid was obtained which decomposed at 300°C. It was soluble in sodium bicarbonate solution and could be precipitated again by acidification.

XV. CHLOROMELAMINES

A. General

In common with the majority of primary and secondary amines melamine reacts with chlorine to form chloroamines.

$$RNH_2 + Cl_2 \rightarrow RNHCl + HCl$$

The "available chlorine" content of these compounds (defined as the chlorine equivalent to one molecule of free chlorine) is in fact double the actual chlorine content of the molecule, as is shown by their reaction with hydriodic acid:

$$RNHCl + 2HI \rightarrow RNH_2 + I_2 + HCl$$

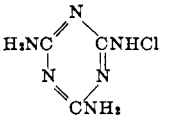
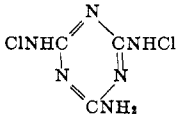
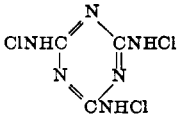
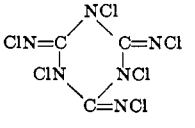
Compare with the reaction:

$$Cl_2 + 2HI \rightarrow I_2 + 2HCl$$

Mono-, di-, tri-, and hexachloromelamines have been described (see table 12). Several methods for their preparation have been reported in the patent literature: (*1*) chlorination in aqueous suspension, (*2*) chlorination in aqueous suspension using hypochlorites, and (*3*) chlorination in suspension in organic solvents.

TABLE 12

Chloromelamines

Compound	Formula	Molecular Weight	Chlorine	Available Chlorine
			per cent	*per cent*
Monochloromelamine		160.6	22.1	44.2
Dichloromelamine		195.0	36.4	72.7
Trichloromelamine		229.5	46.4	92.7
Hexachloromelamine		332.8	63.9	127.8

In chlorination in aqueous suspension (18) the first stage is considered to be the formation of hypochlorous acid:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

The hypochlorous acid then reacts with the melamine:

$$C_3N_3(NH_2)_3 + HOCl \rightarrow C_3N_3(NH_2)_2(NHCl) + H_2O$$

$$C_3N_3(NH_2)_2(NHCl) + HOCl \rightarrow C_3N_3(NH_2)(NHCl)_2 + H_2O$$

$$C_3N_3(NH_2)(NHCl)_2 + HOCl \rightarrow C_3N_3(NHCl)_3 + H_2O$$

Complete chlorination to give hexachloromelamine is difficult in an aqueous route for several reasons.

(*1*) The hydrochloric acid liberated converts part of the melamine into its hydrochloride, which is difficult to chlorinate:

$$C_3H_6N_6 + HCl \rightarrow C_3H_6N_6 \cdot HCl$$

(*2*) As the hydrochloric acid builds up in the reaction mixture, it reacts with the chloromelamine:

$$C_3N_3(NH_2)_2(NHCl) + HCl \rightarrow C_3N_3(NH_2)_3 + Cl_2$$

(*3*) In the presence of alkali the hydrochloric acid is neutralized, but alkali salts of the chloromelamines are also formed:

$$C_3N_3(NH_2)_2(NHCl) + NaOH \rightarrow C_3N_3(NH_2)_2(NNaCl) + H_2O$$

The earlier patents (125, 126, 127, 146) show that the chlorination of melamine in aqueous suspension does not give a chloromelamine containing more than 100 per cent available chlorine even when alkali is present. The usual products obtained approximate to dichloromelamine (available chlorine about 70 per cent) in the absence of alkali, and trichloromelamine (available chlorine about 90 per cent) when alkali is present.

According to Arsem (18) melamine can be chlorinated to yield distinct halogen compounds containing from one to six halogen atoms by operating with a weakly acid solution of hypochlorous acid obtained, for example, by adding sodium hypochlorite solution to melamine and dilute acetic acid, or by chlorinating a suspension of melamine in sodium acetate solution. Further details of this method are given below.

B. Dichloromelamine

The chlorination of melamine in the form of an aqueous slurry is described in several patents (125, 126, 127, 145). According to Muskat (125), chlorine was passed into a melamine slurry (75 g. of melamine per liter) at 25°C. for 2 hr. The white crystalline product contained 74 per cent available chlorine.

A similar white chloromelamine was obtained (127) by chlorinating a melamine slurry (97 g. of melamine per liter) at 0.10°C. with a chlorine rate of 0.75 g./liter/minute for 4 hr. The product contained 73 per cent available chlorine.

C. Trichloromelamine

Chlorination of melamine in aqueous suspension in the presence of lime (126, 127) gave orange-yellow products of active chlorine content approximating to that of trichloromelamine.

An aqueous melamine slurry (65 g. of melamine per liter) containing powdered calcium hydroxide (60 g. per liter) was chlorinated at 13–15°C. at a rate of 0.75 g. of chlorine/liter/minute for 6 hr. (126). The orange-yellow product contained 88.5 per cent available chlorine.

A slurry containing 65 g. of melamine and 58 g. of calcium hydroxide per liter was chlorinated for 2 hr. without cooling (125). The temperature rose to 50°C. The yellow-orange product was substantially free from calcium after washing and contained 100 per cent available chlorine.

Trichloromelamine may be obtained by the reaction of hexachloromelamine, prepared by the use of hypochlorite (see Section XV,E), with the equivalent amount of melamine (18). A mixture of 333 g. of hexachloromelamine and 126 g. of melamine was stirred in 200 ml. of water, and acetic acid was added. Upon heating to 50°C. trichloromelamine was formed. The product had a molecular weight of 229.5 and an available chlorine content of 93 per cent.

D. Monochloromelamine

It is claimed that monochloromelamine may be made by a similar method, by the reaction of 1 mole of hexachloromelamine with 5 moles of melamine. The product obtained had a molecular weight of 160.5 and an available chlorine content of 44.2 per cent.

E. Hexachloromelamine: aqueous route

Melamine (126 g.) was stirred with 2 l. of water and 400 g. of acetic acid at 20°C. While the mixture was stirred and cooled, 475 g. of sodium hypochlorite, as an approximately 5 per cent solution, was added. After stirring for 30 min. the mixture was filtered. Substantially pure hexachloromelamine was obtained as a light, loose, white powder having a yellowish tinge. It had a molecular weight of 333 and an available chlorine content of 128 per cent. The substance can be dried at 80°C.

In a similar way (18) hexachloromelamine was obtained by the direct chlorination at 20°C. of 126 g. of melamine in 10 g. of water containing 860 g. of crystalline sodium acetate. The weight of chlorine used was 440 g.

F. Hexachloromelamine: solvent route

A mixture of 62 g. of melamine suspended in 1 l. of carbon tetrachloride together with 160 g. of sodium carbonate containing "sufficient water to assist the reaction but insufficient to form an aqueous solution in the liquid state" was treated with chlorine at 10°C. for 7 hr. (36). In general, equal mole ratios of alkali and chlorine were used. The yellow product was hexachloromelamine containing 128 per cent available chlorine. It was soluble in carbon tetrachloride. According to this patent attempts to secure compounds containing above 119

per cent available chlorine by chlorinating melamine in aqueous alkaline solution or in carbon tetrachloride in the absence of sodium carbonate at temperatures up to 25°C. have not been successful.

G. Properties of chloromelamines

Di-, tri-, and hexachloromelamines have been described in a document (78) on research work carried out by the I. G. Farbenindustrie. The products differ characteristically in their reactivity and particularly in their solubility in organic solvents. Thus, trichloromelamine is soluble in acetone but insoluble in carbon tetrachloride. Dichloromelamine is insoluble in both solvents, while hexachloromelamine is soluble in both. A compound of chlorine content corresponding approximately to that of trichloromelamine has been described by Muskat and Chenicek (127). It is soluble in triacetin, acetonylacetone, ethyl acetate, water, and aqueous alkali.

The chloromelamines are relatively stable despite their high content of active chlorine.

Hexachloromelamine reacts with certain unsaturated compounds such as styrene, 1-heptene, acrylic ester, methacrylic ester, and cyclohexene to form resins which give up chlorine. The reaction is essentially an addition reaction. In other cases chloromelamines acts as a chlorinating agent. Thus, hexa- and trichloromelamine give dichloromelamine and chloroacetone if allowed to stand in acetone; the reaction takes place more quickly in boiling acetone.

XVI. BROMO- AND IODOMELAMINES

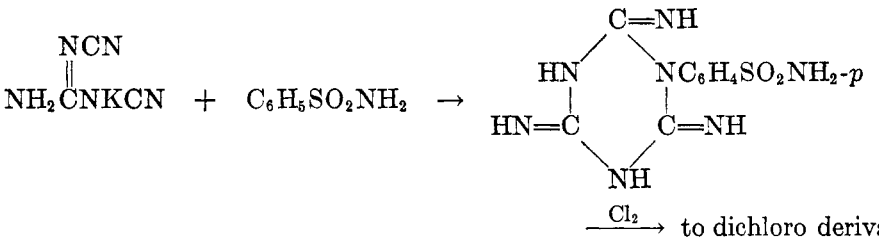
The preparation of these compounds is carried out in a manner analogous to that used for the chloromelamines (127): e.g., an aqueous slurry containing 100 g. of melamine per liter was treated dropwise with bromine at 15–20°C. until the color of the latter was no longer destroyed. The product contained 112 per cent of active bromine.

In another experiment 960 g. of bromine in carbon tetrachloride was added over a period of 5 hr. to 126 g. of melamine and 320 g. of sodium carbonate in 500 ml. of carbon tetrachloride. The product was filtered and the filtrate evaporated to dryness, giving a yellow solid containing 158 per cent of active bromine.

The reaction between 260 g. of iodine in 10 per cent sodium hydroxide and 50 g. of melamine in 1 l. of water at 50–60°C. for 4 hr. gave a product containing 128 per cent of active iodine.

XVII. CHLORINATED MELAMINE DERIVATIVES

Chlorinated monoarylisomelamines have been reported by Nagy and Kaiser (131). The chlorination of *p*-sulfonamidophenylisomelamine, prepared from dicyanoguanidine and sulfanilamide, at room temperature until an excess of chlorine was present gave a light yellow solid containing 38.6 per cent of chlorine (slightly less than the theoretical amount—44 per cent—for a dichloro compound).



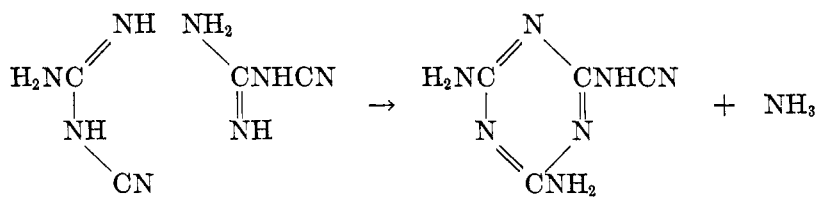
The high stability of this compound was shown by refluxing it with water; the loss of chlorine after 3 hr. was 2.6 per cent, whereas the corresponding normal chloro derivative lost 92.5 per cent of chlorine when similarly treated.

Similar chlorinated products from *p*-phenylenediisomelamine and phenylisomelamine have been reported: e.g., 4.04 parts of phenylisomelamine in 50 parts of water containing 5.3 parts of sodium carbonate was chlorinated at 6–8°C. On acidification with acetic acid there was obtained a pink precipitate containing 35 per cent chlorine; the solid melted at 168–170°C. with decomposition.

When 235 g. of melam in 4 l. of water and 450 g. of acetic acid was treated with 675 g. of sodium hypochlorite at 20°C., nonachloromelam was obtained as a buff-colored powder with an active chlorine content corresponding to the formula $C_6N_{11}Cl_9$.

XVIII. CYANOMELAMINES AND GUANYLMELAMINES

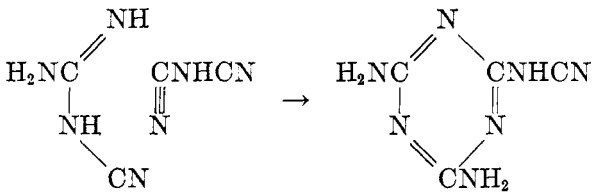
Cyanomelamine has not been obtained from melamine directly; it is, however, a by-product formed in the reaction of dicyandiamide in ammonia at temperatures below 180°C. (99). Thus 200 g. of dicyandiamide in 300 g. of ammonia was heated for 2 hr. at 150°C. at a pressure of 100–125 atm.; on venting the ammonia the resulting product contained 6.9 per cent of cyanomelamine and 5.9 per cent of melamine. The mixture was extracted with acetone to remove dicyandiamide; the residue was extracted with methanol and taken up in water. Cyanomelamine was precipitated as a purple copper complex by adding copper ammonium sulfate solution. Decomposition of the copper complex by treatment with hydrochloric acid gave free cyanomelamine, which was further purified by solution in alkali and reprecipitation with acid.



N^2-Cyanomelamine

Cyanomelamine may be prepared by heating dicyandiamide and sodium dicyanimide in methoxyethanol containing an excess of potassium hydroxide (85). Thus 25.0 g. of 85 per cent potassium hydroxide was dissolved in 1125 ml. of methoxyethanol, and 252 g. of dicyandiamide and 240 g. of sodium dicyanimide

(94 per cent) were added. The mixture was heated at reflux (130°C.) for 2.5 hr. A yield of 321 g. (85 per cent) of N^2-cyanomelamine was obtained.



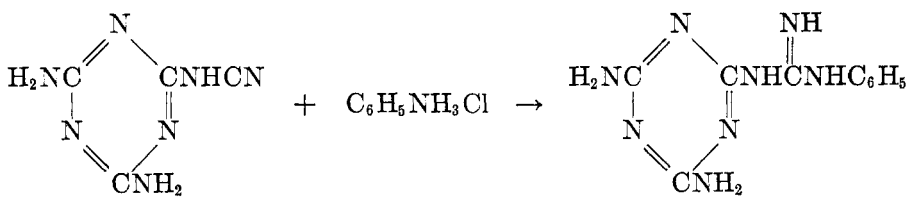
N^2-Cyanomelamine

It is considered that the direct preparation of cyanomelamine from dicyandiamide and ammonia may arise from some conversion of dicyandiamide into ammonium dicyanimide:

$$NH_2C(=NH)NHCN \rightarrow CNNHCN + NH_3$$

The reaction with dicyandiamide would then proceed as above. In general, however, the reaction conditions are those in which melamine is formed from dicyandiamide, and at higher temperatures melamine predominates.

Cyanomelamine is a white infusible material, very sparingly soluble in water and readily soluble in alkali. It can be crystallized from a 25 per cent solution of ethoxyethanol in water (75 per cent), to give fine colorless needles. It can be distinguished from ammeline and ammelide by the formation of a copper complex with copper ammonium sulfate, and by the formation of guanylmelamines with amine hydrochlorides (5, 8, 86, 114). Thus, when N^2-cyanomelamine and aniline hydrochloride were heated in glycol at 165°C. for 10 min., ω-phenylguanylmelamine, m.p. 240–242°C., was formed in 91 per cent yield.



N^2-Cyanomelamine ω-Phenylguanylmelamine

Other guanylmelamines prepared in this way are given in table 13.

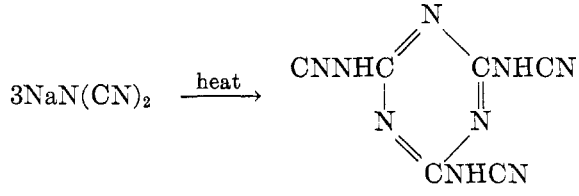
TABLE 13

Guanylmelamines from cyanomelamine and amine hydrochlorides

Amine Hydrochloride	Product
Aniline	ω-Phenylguanylmelamine
Methylaniline	ω-Methyl-ω-phenylguanylmelamine
Sulfanilamide	*p*-Sulfamyl-ω-phenylguanylmelamine
Benzylamine	ω-Benzylguanylmelamine
Cyclohexylamine	ω-Cyclohexylguanylmelamine
Dodecylamine	ω-Dodecylguanylmelamine
2,4-Dichloroaniline	2,4-Dichloro-ω-phenylguanylmelamine
p-Chloroaniline	*p*-Chloro-ω-phenylguanylmelamine
Butylamine	ω-Butylguanylmelamine
p-Trifluoromethylaniline	*p*-Trifluoromethyl-ω-phenylguanylmelamine

According to a recent patent (9) guanylmelamines are prepared from dicyandiamide by heating with an anhydrous hydrogen halide at 40–180°C.

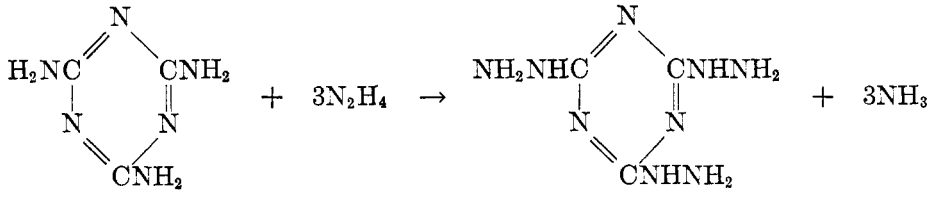
Tricyanomelamine has been obtained by heating sodium dicyanimide to a dark red heat (122) and acidifying the product with acetic acid.



Tricyanomelamine

XIX. CONDENSATION OF MELAMINE WITH HYDRAZINE

Melamine condenses with hydrazine to form triaminomelamine, m.p. 287°C. The reaction can be carried out by heating melamine with five molecular proportions of hydrazine hydrate at 150°C. for 5 hr. (180).



When shaken in hydrochloric acid with benzaldehyde, triaminomelamine yields a tribenzylidene derivative (59, 120).

XX. APPLICATIONS OF MELAMINE AND ITS DERIVATIVES

Only applications of melamine products other than condensates of melamine with formaldehyde will be considered in this review.

A. Melamine

Melamine has recently been suggested for use as an inhibitor of corrosion. According to one patent (124) 15–250 p.p.m. of melamine is added to hydrogen sulfide-containing brines used in oil purification to prevent the corrosion of pipelines. The metal developed a tenacious coating which was resistant to hydrogen sulfide. Melamine and its derivatives have been mentioned in several patents as inhibitors for addition to detergent compositions for the prevention of tarnish when cleaning articles made of German silver. Up to 1 per cent of melamine, methylmelamine, or methylolmelamine is added (40). The dark stain obtained when the articles are washed without an inhibitor is reduced to a very slight tarnish when melamine is present.

Melamine, dicyandiamide, and biguanide are used with oxalic acid to form blowing agents for the making of expanded plastics (28).

B. Melamine salts

Melamine hydrochloride is used in fused salt baths for the heat treatment of metals (32); from 0.01 to 10 per cent of the hydrochloride is added to the mixture of sodium chloride and potassium chloride used.

The melamine salt of penicillin (35) is said to be of value in animal feeds because of its low solubility, which helps to retain the penicillin in the body.

The double sulfate of melamine and dodecylamine (m.p. 300°C.) has been patented for use in cosmetics (163).

The salts of melamine with nitrophenols are claimed to be of value as insecticides (121). Unlike simple nitrophenols, they do not burn with explosive violence.

A patent application (7) mentions the use of melamine pyrophosphate, prepared from melamine hydrochloride and sodium pyrophosphate, in fireproofing.

C. Alkyl-, aryl- and acylmelamines

Butylmelamine was stated (78) to give formaldehyde resins with very good properties.

Mono- and diphenylmelamines have been mentioned for use (78) in the preparation of plastics, and in particular for the preparation of lacquer resins of the Naprenal type.

N^2,N^2-Diallylmelamine is commercially available (13). It reacts with neutral and alkaline formaldehyde to give methylol derivatives, and in the presence of an azo type or peroxide catalyst it polymerizes through its double bonds to give a hard, cross-linked polymer. It has been found to be of particular utility in a pulp preform moulding process, in a number of other moulding applications, and in surface-coating resins. Like melamine (58), it condenses with alkylene oxides to form water-soluble polyethers with surface-active properties.

The hydroxyarylmelamines obtained by the alkylation of melamine with *p*-aminophenols (31, 43) are stated to have uses in insecticides, fungicides, pharmaceuticals, plasticizers, and as intermediates for formaldehyde condensation.

Triethylmelamine has chemotherapeutic properties. The chemotherapeutic properties of triethylenemelamine in the treatment of malignant diseases have been evaluated by Rundle and Barton (157). It is claimed to be useful for treating Hodgkin's disease, malignant lymphoma, and carcinoma of the ovary.

Diethylenetrimelamine is recommended for the manufacture of flameproofing materials, fungicides, insecticides, and synthetic resin coatings (52).

Tri-*tert*-alkylmelamines (83) are useful in the preparation of synthetic resins and surface-active agents.

Methyl- and ethylisomelamines are used in ion-exchange resins, as curing agents for resins, and as assistants in the dyeing of textiles (130).

The use of tristearylmelamine in water-repellent finishes for fabrics and polishing waxes has been mentioned (56).

One patent (66) mentions tri(tall oil) melamine as a water repellent for wood products.

p-Aminobenzenesulfonylmelamine has bactericidal properties. It can be used

as an intermediate in the preparation of pharmaceuticals and azo dyes. Its value as an antirheumatic has been claimed (153).

Guanylmelamines are claimed to be useful as flameproofing agents and as chemical intermediates for the preparation of dyestuffs and plastics (86, 114).

D. Melamine complexes

Condensates obtained from melamine and glycidol (57) are stated to be of use as textile and leather assistants and as anticrease and mercerizing agents.

The complex prepared from melamine and phosphorus pentoxide (115) has potential use in fireproofing; several methods of applying the material are described (133). In one example 15 per cent of the melamine-phosphorus pentoxide complex was ground to 325 mesh and mixed with a phenol-formaldehyde resin. A material used in coating metal panels to prevent afterflame and afterglow contains 30 per cent of this complex.

The crystalline double compound formed from melamine and glucose (148) does not appear to have found applications, e.g., in sugar purification, but compounds obtained by heating hexoses in the molten state with urea, thiourea, melamine, or guanidine in the presence of a dehydrating agent are claimed to be effective for the creaseproofing and shrinkproofing of textile materials and for the waterproofing of paper and cardboard (119).

E. Chloromelamines

The chloromelamines behave as chloroamides. They are relatively stable despite their high content of active chlorine, and they therefore find use as chlorinating agents. The active chlorine content of hexachloromelamine (128 per cent) exceeds that of elementary chlorine.

Possible uses (18) of chloromelamines are as antiseptics, disinfectants, oxidizing agents, oxidation catalysts, drying agents for paints, oils, and synthetic resins, and intermediates for the preparation of bleaching agents. Price considerations make it unlikely that they will find use in bulk quantities in the fields of water treatment, textile bleaching, and agricultural antiseptics. They are, however, used in surgical antiseptics and find military uses in the sterilization of drinking water in the field. Dilute aqueous solutions of chloromelamines are more effective than hypochlorite solutions for use in sterilizing, since they have a greater stability and are effective against a greater variety of bacteria. They are the only rinses found so far that are effective against the amoebic cyst. It has been reported (16) that trichloromelamine is being used as a rinse by the U. S. armed forces. It is also used for treating fruits and vegetables in order to prevent decay during shipment and storage (145, 146).

Marks (116) has described the use of a chloromelamine solution for the sterilization of ion-exchange bodies in water softeners. The chloromelamine solution, containing 20–100 p.p.m. of available chlorine, is passed through the bed at the time of regeneration.

In the medical field, the literature would indicate that the principal applications at present of the chloromelamines lie in the range of textile-sterilizing

agents, where these compounds are preferred as they have a high available chlorine content, are stable on the cloth for considerable periods, have no bleaching action, and may conveniently be applied from carbon tetrachloride solution in the course of the normal dry-cleaning operation (128). Another patent (169) describes a stable melamine composition for bleaching or sterilizing, or as a germicidal agent, obtained from a melamine-chloromelamine mixture having an available chlorine content of over 100 per cent, which is dissolved in alkaline agents of pH 10 or higher in combination with one or more detergents.

Paden and MacLean (139) have described a germicidal composition containing chloromelamine (containing one to three chlorine atoms per molecule) and potassium iodide (up to 2 per cent of the available chlorine). Chlorinated derivatives of melamine, e.g., chlorinated arylisomelamines, are used for the same purpose (128).

A patent (131) also describes a range of chlorinated isomelamines (see page 162). They contain 25–40 per cent of chlorine and are stable at temperatures below their decomposition points. They are difficultly soluble in water and therefore useful in the sterilization of water, where the accidental addition of excess reagent can do no harm.

The authors wish to thank the Directors of British Oxygen Research and Development Ltd. for permission to publish this review.

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