

PATENT SPECIFICATION

(11) 1301390

1301390

NO DRAWINGS

- (21) Application No. 50489/70 (22) Filed 23 Oct. 1970
 (31) Convention Application Nos. 869 901 and 869 902
 (32) Filed 27 Oct. 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 29 Dec. 1972
 (51) International Classification C07D 55/12
 (52) Index at acceptance
 C2C 175—192—285 214 246 247 250 252 25Y 29X
 29Y 303 30Y 69Y 791 797 79Y ZF
 (72) Inventors WILLIAM LOWRY HOWARD, HERSHEL BEEBE
 PRINDLE, JACK ALLEN McELREATH and
 DAVID RAY ELLIOTT



(54) STABILIZED BIOCIDAL COMPOSITIONS OF HEXAMETHYLENETETRAMINE ADDUCTS AND PREPARATION THEREOF

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a stabilized biocidal composition and the preparation thereof.

Adducts of certain unsaturated olefinic or acetylenic halides with hexamethylenetetramine are effective germicides when present in concentrations as low as 0.01 per cent in water-containing organic mixtures such as, for example, emulsified cutting oils, latexes, latex paints, aqueous adhesives, hydraulic fluids and pulp dispersions used in paper-making.

In particular, adducts formed by the reaction of hexamethylenetetramine with an olefinically or acetylenically unsaturated bromide, chloride, or iodide, wherein the carbon chain contains a maximum of about eight carbon atoms, exhibit the antimicrobial activity of the unsaturated halide moiety as well as other valuable properties not exhibited by the unsaturated halide.

Unsaturated haloalkylcarbons which form adducts with hexamethylenetetramine having particularly high antimicrobial activity are dihaloalkenes and haloalkynes such as propargyl bromide, propargyl chloride, 1,3-dichloropropene, 2,3-dichloropropene, 3,3-dichloropropene, diiodoacetylene, and 1,4-dichloro-2-butyne.

Although, as set forth hereinbefore, these

adducts are very effective antimicrobials, under certain conditions it has been found that the compounds may undergo spontaneous exothermic decomposition. This phenomenon, if it occurs, has arisen usually in those instances where the mass of an adduct is such that there is inadequate means for heat transfer from the interior of the mass to the surrounding environment. Generally, such sporadic spontaneous decomposition has been found to occur where packages or large compact piles of the compound have been stored or accumulated such as is commonly practised in the warehousing or other inventory storage of materials. Heretofore, means for providing heat transfer to eliminate or suppress the decomposition primarily have been directed to limiting the size of the mass of the biocidal adduct in at least one dimension to provide a short heat transfer path which prevents the development of a detrimentally large temperature difference between the interior of the mass and the environment, e.g. the atmosphere and walls of a package. Conveniently, small or thin elongated shaped packages wherein large masses were not accumulated in a given location have been found to be suitable heretofore for storage.

It has now been found, and the discovery forms the basis of the present invention that the hexamethylenetetramine-unsaturated aliphatic halide adducts can be stabilized by mixing a suppressor additive either with the product or with the reactants so that the adduct is formed in the presence of the adduct. The invention therefore concerns the stabilized adducts and to the method of making the stabilized adducts. The stabilized adducts of the invention contain a suppressor additive selected from urea, biuret, 1 or 2 carbon aliphatic aldehyde polymers, am-

[Price 25p]

monium or alkali metal bicarbonates, ammonium or alkali metal salts of 2 to 8 carbon aliphatic polycarboxylic acids, and alkaline earth metal oxides and carbonates in a proportion to suppress the self-propagating exothermic decomposition of the adducts. Usually the stabilized adduct contains 5 to 90 and preferably 15 to 45 weight per cent of the suppressor additive. Preferred compositions of the invention are comprised of 55 to 95 weight per cent of the adduct of equimolar portions of hexamethylenetetramine and 1,3-dichloropropene and 45 to 5 weight per cent of sodium bicarbonate or paraformaldehyde. More preferably, the compositions comprise from 95 to 75 weight per cent of the adduct of hexamethylenetetramine and 1,3-dichloropropene and from 5 to 25 weight per cent of paraformaldehyde.

As previously indicated the composition of the invention can be prepared either by mixing the adduct and the suppressor additive or by forming the adduct in the presence of the adduct, usually in the presence of an inert carrier liquid. Thus, particularly good results are obtained by mixing the suppressor additive with hexamethylenetetramine in the presence of an inert carrier liquid, the unsaturated aliphatic halide added with stirring to form the adduct and the stabilized adduct separated from the carrier liquid. The reaction proceeds at a good rate at temperatures of 25 to 75°C. preferably 50 to 70°C. with stirring for 2 to 40 hours and preferably 10 to 16 hours after the halide addition is completed. Usually the reaction mixture is in the form of a slurry containing preferably 20 to 35 weight per cent of solids and the resulting solid stabilized adduct separated from the liquid carrier and dried at 25 to 65°C. under subatmospheric pressure.

The drying of the solid composition is usually carried out within a temperature range of from 25°C. to 65°C. at an absolute pressure of from 2 to 27 inches (51 to 685 mm) of mercury but preferably at a temperature of from 40°C. to 55°C. at an appropriately reduced pressure in the range referred above. These conditions are not critical but assure rapid carrier liquid removal without encountering adduct decomposition during the drying step.

Carrier liquids ordinarily employed in the practice of the present invention are those which are solvents for the hexamethylenetetramine and the olefinic halide or acetylenic halide, and which do not undergo reaction with these reactants, the suppressor additive, the adduct or the final product composition. Conveniently, relatively low boiling organic liquids such as the halogenated alkanes, e.g. chloroform, methylene chloride and carbon tetrachloride, methanol, ethanol, tetrahydrofuran and dioxane are employed.

Representative materials which have been

found to be particularly suitable for use as suppressor additives in the present compositions are paraformaldehyde, sodium bicarbonate, ammonium bicarbonate, urea, magnesium oxide, ammonium citrate, biuret and s-trioxane.

Example I

A 2-gallon (7.6 l) glass lined kettle was fitted with an adjustable speed agitator and mechanical seal, and an automatic temperature control. 681 grams of hexamethylenetetramine, 406 grams of sodium bicarbonate and 2790 grams of methylene chloride were introduced into the reactor. These quantities were calculated to provide a final slurry having a total solids content of 30 weight percent and a product composition containing 25 weight percent of sodium bicarbonate.

The agitator was operated at 150 rpm and the reaction mixture heated to 60°C.

A mixture containing 24.2 percent 1,2-dichloropropane and 75.8 percent 1,3-dichloropropene was introduced into the top of the reactor at a feed rate of 5 milliliters per minute and 710 grams of the olefinic halide reactant was added over a period of 2 hours. This quantity of the olefinic halide adduct-former provided 5 weight percent excess of the 1,3-dichloropropene required stoichiometrically for formation of a 1:1 hexamethylenetetramine:1,3-dichloropropene adduct.

The resulting mixture was maintained at 60°C. under agitation for a period of 6 hours. Ionic chloride analysis of a product sample after this reaction period showed 92 percent conversion to the adduct. Agitation at the indicated reaction temperature was continued for an additional two hours after which time the product mass was removed from the reactor.

The solid product composition was separated from the carrier liquid and dried at a temperature of 60°C. at an absolute pressure of 27 inches (685 mm) mercury for 8 hours.

Product yield was substantially quantitative. The resulting product was a white to cream colored particulate solid having a bulk density of from 0.6—0.8 gram/cubic centimeter.

The suppressor activity of the additive containing composition was determined by placing 8 grams of the composition along a 4 inch (10.1 cm) section of an insulated trough 6 inches (15.2 cm) long. The remaining 2 inch (5.1 cm) section of the trough was loaded with 4 grams of unstabilized 1:1 hexamethylenetetramine:1,3-dichloropropene adduct. The heated tip of an electric soldering gun was inserted into the end of the section of adduct which was remote from the interface of the two samples to initiate exothermic decomposition of the adduct. The behavior of both the adduct and the suppressor additive containing composition was observed.

Rapid propagation through the length of the

unstabilized adduct with complete degradation occurred. The decomposition stopped completely at the interface of the adduct and the suppressor additive containing composition. No visible decomposition of the latter composition could be seen.

Example 2

A 5-neck, 2-liter flask equipped with a chilled water condensor with drying tube, dropping funnel, heating mantel with automatic heat control, thermometer and air-driven stirrer was used as a reactor. Predetermined quantities of hexamethylenetetramine, a suppressor additive material and methylene chloride were added to the reactor and the solution was heated to 40°C. A mixture containing 24.2 percent, 1,2-dichloropropane and 75.8 percent 1,3-dichloropropene, in an

amount sufficient to provide 10 weight percent excess of that required stoichiometrically for preparation of a 1:1 hexamethylenetetramine: 1,3-dichloropropene adduct, was added slowly through the dropping funnel. Following completion of the olefinic halide addition, the reaction mixture was agitated while maintaining the reaction temperature at 40°C. until an ionic chloride analysis corresponding to at least 94 percent conversion to the adduct was reached.

The slurry was removed from the reactor, the solid product composition separated from the carrier liquid and dried at a temperature of 60°C. under a pressure of 27 inches (685 mm) mercury for a period of from 8 to 15 hours.

Table I summarizes the mix components, quantities, and reaction conditions employed.

TABLE I

Run No.	Mix Components		Suppressor Additive			Solids in pdt. slurry (%)	Reaction Conditions		
	Hexa-methylene-tetramine (grams)	1,3-di-chloro-propene (grams)	(type)	(grams)	(% of com-position)		CH ₂ Cl ₂ (grams)	1,3-dichloro-propene feed time (hr.)	Reaction Period (hr.)*
1	134	116.5	NaHCO ₃	42.5	15	659	30	1	31
2	134	116.5	Urea	42.5	15	659	30	1	31
3	134	116.5	MgO	42.5	15	659	30	2	31
4	279	243	NaHCO ₃	167	25	2220	24	3.5	16.5
5	134	117.5	Biuret	80	25	746	31	2	18.5
6	134	117.5	MgO	80	25	746	31	2	18.5
7	134	116.5	Urea	80	25	746	30	1.5	31.5
8	13.95	11.05	NaHCO ₃	225	90	584	30	0.17	31.5
9	13.95	11.05	Urea	225	90	584	30	0.17	31.5
10	13.95	11.05	MgO	225	90	584	30	0.17	31.5

* after 1,3-dichloropropene addition was completed.

Each of the resulting compositions was tested employing the trough test described in Example 1. In every case, propagation of the adduct decomposition stopped at the interface of the unstabilized adduct and the stabilized adduct of the invention.

In a similar manner, a number of additive-containing adduct compositions are prepared. The weight proportions of the suppressor additive and adduct in the blended compositions are summarized in Table II.

TABLE II

Composition	Hexamethylenetetramine Adduct		Suppressor Additive	
	(aliphatic halide moiety) (wt.%)		(Type)	(wt.%)
1	1,3-dichloropropene	80	ammonium bicarbonate	20
2	propargyl bromide	75	dibasic ammonium citrate	25
3	diiodoacetylene	85	s-trioxane	15
4	1,3-dichloropropene	90	paraformaldehyde	10
5	propargyl chloride	70	potassium bicarbonate	30
6	1,3-dichloropropene	60	calcium oxide	40
7	propargyl bromide	55	sodium bicarbonate	45
8	2,3-dichloropropene	75	sodium bicarbonate	25
9	1,3-dichloropropene	40	calcium carbonate	60

Each of the resulting compositions are found to exhibit a markedly increased resistance to self-propagated exothermic decomposition over that shown by the adduct itself.

Example 3

167 pounds (75.5 kg) of hexamethylenetetramine, 100 pounds (43.3 kg) of NaHCO_3 , and 900 pounds (407 kg) of methylene chloride were loaded into a 200 gallon (758 l) glass-lined reactor. The resulting mixture was stirred by a methanical agitator at 60 revolutions per minute and the reactor purged three times with nitrogen. The agitated mass was heated to 65°C. and maintained at this temperature for two hours during which time 92 pounds (41.6 kg) of a mixture containing 24.2 percent 1,2-dichloropropane and 75.8 percent 1,3-dichloropropene was added thereto. The reaction mass was digested for two hours at 65°C. and an additional 90 pounds (40.7 kg) of the 1,2 - dichloropropane - 1,3-dichloropropene mixture was added over a two hour period while maintaining a temperature of 65°C. in the stirred reaction mixture.

This reaction mixture was calculated to provide a slurry having a 30 weight per cent solids content, a suppressor additive content of 25 per cent based on the total composition weight of solids in the slurry. The 1,3-dichloropropene was used in an amount to provide 105 weight percent of that required stoichiometrically for a 1:1 hexamethylenetetramine: 1,3-dichloropropene adduct.

Following completion of the 1,3-dichloropropene reactant addition, the reaction mixture was heated, under agitation, for an additional 6 hours at the 65°C. temperature.

The product slurry was transferred to a rotary vacuum dryer and dried for 14 hours under an absolute pressure of 25 inches (635 mm) of mercury. The water jacket temperature of the dryer during the drying operation was maintained at 75°C.

The resulting dried composition was recovered. Analysis indicated conversion to the adduct was about 95 percent.

Samples of the stabilized adduct product composition did not undergo any visible decomposition when subjected to the trough test.

The following example illustrates the improved yields provided by the process of the present invention.

Example 4

A. Stabilized Adduct According to the Known Art

Into a reactor was placed 4000 pounds (1813 kg) of hexamethylenetetramine in 16000 pounds, 7260 kg) of methylene chloride and the reactor and contents were then purged with nitrogen gas and heated to 65°C. To this was added, over a six hour period 2960 pounds (1795 kg) of a mixture containing 20% 1,2-dichloropropane and 80% 1,3-dichloropropene. Following this addition the reaction mixture was digested for six hours at 65°C. and then cooled to 30°C. and finally transferred to a rotary vacuum dryer and dried for 10 hours using a liquid heat exchange medium maintained at 80°C. and at an absolute pressure of 25 inches (635 mm) of mercury. The product analysis showed 91.6 percent conversion of hexamethylenetetramine to active adduct.

B. Preparation According to the Present Invention

Into a reactor was placed 3000 pounds (1358 kg) of hexamethylenetetramine, 1800 pounds (816 kg) of sodium bicarbonate and 16500 pounds (7475 kg) of methylene chloride. The reactor and contents were then purged with nitrogen gas and heated to 65°C. To this was added 2970 pounds (1347 kg) of a mixture containing 20 percent 1,2-dichloropropane and 80 percent 1,3-dichloropropene over a six hour period. Following this addition the reaction mixture was digested for six hours at 65°C. and then cooled to 30°C. and finally dried in a rotary vacuum dryer for 10 hours using a liquid heat exchange medium maintained at 80°C. and at an absolute pressure of 25 inches (635 mm) of mercury. The analysis of this product showed 97.9 percent conversion of hexamethylenetetramine to the active adduct.

In the above two experiments the relative proportions of hexamethylenetetramine to 1,3-dichloropropene were identical.

A series of similar runs was made in the

manner of Example 4A (six runs) and Example 4B (six runs) which gave average conversions of 90.90 and 95.75, respectively.

Samples of hexamethylenetetramine - 1,3-dichloropropene adduct which were prepared in the manner of Example 4A and 4B above were dried to constant weight under vacuum. A weighed quantity (Sample 1) of the adduct prepared in the manner of Example 4A was placed in a flat dish. A second weighed quantity (Sample 2) of the same adduct preparation was dry-blended thoroughly with an amount of sodium bicarbonate to provide a sample containing 25% by weight of that suppressor additive and placed in a similar container. A third weighed quantity (Sample 3) of the adduct prepared in the manner of Example 4B (which contained 27% by weight sodium bicarbonate by analysis) was placed in a third similar container. All three samples in their containers were placed in an atmosphere maintained at a constant relative humidity of 54 percent. Each container was weighed at hourly intervals. Results of this test are shown in tabular form below.

Time (hrs)	Sample 1		Sample 2		Sample 3	
	Wt (g)	% water	Wt (g)	% water*	Wt (g)	% water*
0	27.67	—	27.80	—	28.00	—
1	28.23	2.02	28.23	2.06	28.20	0.98
2	28.42	2.71	28.35	2.64	28.25	1.22
3	28.52	3.07	28.42	2.97	28.27	1.32
4	28.62	3.44	28.48	3.26	28.28	1.37
5	28.70	3.73	28.48	3.26	28.28	1.37

* % water is based on actual weight of adduct present.

WHAT WE CLAIM IS:—

1. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct containing a suppressor additive selected from urea, biuret, a 1 or 2 carbon aliphatic aldehyde polymer, an ammonium or alkali metal bicarbonate, an ammonium or alkali metal salt of a 2 to 8 carbon aliphatic polycarboxylic acid or an alkaline earth metal oxide or carbonate in a proportion to suppress the self-propagating, exothermic decomposition of the adduct.

2. An adduct as claimed in claim 1 containing 5 to 90 weight percent of the additive.

3. An adduct as claimed in claim 1 containing 15 to 45 weight percent of the additive.

4. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct containing

a suppressor additive selected from urea, biuret, a 1 or 2 carbon aliphatic aldehyde polymer, an ammonium or alkali metal bicarbonate or an ammonium or alkali metal salt of a 2 to 8 carbon aliphatic polycarboxylic acid in a proportion to suppress the self-propagating, exothermic decomposition of the adduct.

5. An adduct as claimed in claim 4 containing 5 to 90 weight percent of the additive.

6. An adduct as claimed in claim 4 containing 15 to 45 weight percent of the additive.

7. An adduct as claimed in any one of claims 4 to 6 wherein the adduct is 1:1 hexamethylenetetramine:1,3-dichloropropene.

8. An adduct as claimed in any of claims 4 to 7 comprising 55 to 95 weight percent of the adduct of equi-molar portions of hexa-



**B. Preparation According to the Present
Invention**

5 Into a reactor was placed 3000 pounds (1358 kg) of hexamethylenetetramine, 1800 pounds (816 kg) of sodium bicarbonate and 16500 pounds (7475 kg) of methylene chloride. The reactor and contents were then purged with nitrogen gas and heated to 65°C. To this was added 2970 pounds (1347 kg) of a mixture containing 20 percent 1,2-dichloropropane and 80 percent 1,3-dichloropropene over a six hour period. Following this addition the reaction mixture was digested for six hours at 65°C. and then cooled to 30°C. and finally dried in a rotary vacuum dryer for 10 hours using a liquid heat exchange medium maintained at 80°C. and at an absolute pressure of 25 inches (635 mm) of mercury. The analysis of this product showed 97.9 percent conversion of hexamethylenetetramine to the active adduct.

15 In the above two experiments the relative proportions of hexamethylenetetramine to 1,3-dichloropropene were identical.

25 A series of similar runs was made in the

manner of Example 4A (six runs) and Example 4B (six runs) which gave average conversions of 90.90 and 95.75, respectively.

Samples of hexamethylenetetramine - 1,3-dichloropropene adduct which were prepared in the manner of Example 4A and 4B above were dried to constant weight under vacuum. A weighed quantity (Sample 1) of the adduct prepared in the manner of Example 4A was placed in a flat dish. A second weighed quantity (Sample 2) of the same adduct preparation was dry-blended thoroughly with an amount of sodium bicarbonate to provide a sample containing 25% by weight of that suppressor additive and placed in a similar container. A third weighed quantity (Sample 3) of the adduct prepared in the manner of Example 4B (which contained 27% by weight sodium bicarbonate by analysis) was placed in a third similar container. All three samples in their containers were placed in an atmosphere maintained at a constant relative humidity of 54 percent. Each container was weighed at hourly intervals. Results of this test are shown in tabular form below.

Time (hrs)	Sample 1		Sample 2		Sample 3	
	Wt (g)	% water	Wt (g)	% water*	Wt (g)	% water*
0	27.67	—	27.80	—	28.00	—
1	28.23	2.02	28.23	2.06	28.20	0.98
2	28.42	2.71	28.35	2.64	28.25	1.22
3	28.52	3.07	28.42	2.97	28.27	1.32
4	28.62	3.44	28.48	3.26	28.28	1.37
5	28.70	3.73	28.48	3.26	28.28	1.37

* % water is based on actual weight of adduct present.

WHAT WE CLAIM IS:—

1. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct containing a suppressor additive selected from urea, biuret, a 1 or 2 carbon aliphatic aldehyde polymer, an ammonium or alkali metal bicarbonate, an ammonium or alkali metal salt of a 2 to 8 carbon aliphatic polycarboxylic acid or an alkaline earth metal oxide or carbonate in a proportion to suppress the self-propagating, exothermic decomposition of the adduct.

2. An adduct as claimed in claim 1 containing 5 to 90 weight percent of the additive.

3. An adduct as claimed in claim 1 containing 15 to 45 weight percent of the additive.

4. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct containing

a suppressor additive selected from urea, biuret, a 1 or 2 carbon aliphatic aldehyde polymer, an ammonium or alkali metal bicarbonate or an ammonium or alkali metal salt of a 2 to 8 carbon aliphatic polycarboxylic acid in a proportion to suppress the self-propagating, exothermic decomposition of the adduct.

5. An adduct as claimed in claim 4 containing 5 to 90 weight percent of the additive.

6. An adduct as claimed in claim 4 containing 15 to 45 weight percent of the additive.

7. An adduct as claimed in any one of claims 4 to 6 wherein the adduct is 1:1 hexamethylenetetramine: 1,3-dichloropropene.

8. An adduct as claimed in any of claims 4 to 7 comprising 55 to 95 weight percent of the adduct of equi-molar portions of hexa-



methylenetetramine and 1,3-dichloropropene and 45 to 5 weight percent of sodium bicarbonate or paraformaldehyde.

5 9. An adduct as claimed in claim 8 which comprises 75 weight percent of said adduct and 25 weight percent sodium bicarbonate.

10 10. An adduct as claimed in claim 8 which comprises 95 to 75 weight percent of said adduct and 5 to 25 weight percent of paraformaldehyde.

15 11. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct containing a suppressor additive selected from urea, biuret, a 1 or 2 carbon aliphatic aldehyde polymer, an ammonium or alkali metal bicarbonate or an ammonium or alkali metal salt of a 2 to 8 carbon aliphatic polycarboxylic acid or an alkaline earth metal oxide in a proportion to suppress the self-propagating, exothermic decomposition of the adduct.

20 12. An adduct as claimed in claim 11 which comprises 10 to 95 weight percent of a hexamethylenetetramine-unsaturated aliphatic halide adduct and 90 to 5 weight percent of an alkaline earth metal oxide.

25 13. An adduct as claimed in claim 12 wherein the adduct is 1:1 hexamethylenetetramine:1,3-dichloropropene adduct and the suppressor additive is magnesium oxide.

30 14. A process for the manufacture of stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct which process comprises mixing a suppressor additive with the adduct in a proportion to suppress the self-propagating exothermic decomposition of the adduct.

35 15. A process as claimed in claim 14 which process comprises mixing the suppressor additive with hexamethylenetetramine in an inert carrier liquid, adding the unsaturated aliphatic

halide to the mixture with stirring to form the adduct and separating the stabilized adduct from the carrier liquid.

45 16. A process as claimed in claim 15 wherein the unsaturated aliphatic halide is added at a temperature of 25 to 75°C, and the stirring and temperature maintained for an additional 2 to 40 hours.

50 17. A process as claimed in claim 15 wherein the unsaturated aliphatic halide is added at a temperature of 50 to 70°C, and the stirring and temperature maintained for an additional 10 to 16 hours.

55 18. A process as claimed in any one of claims 15 to 17 wherein the inert carrier liquid is employed in a proportion to provide a slurry containing 20 to 35 weight percent solids.

60 19. A process as claimed in any one of claims 16, 17 or 18 wherein the stabilized adduct is dried at a temperature of 25 to 65°C, at a pressure of from 51 to 685 mm. of mercury.

65 20. A process as claimed in claim 19 wherein the stabilized adduct is dried at a temperature of 40 to 55°C.

70 21. A process for the manufacture of a stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct substantially as hereinbefore described in any one of the Examples.

22. A stabilized hexamethylenetetramine-unsaturated aliphatic halide adduct whenever produced by a process as claimed in any one of claims 14 to 21.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1.
Chartered Patent Agents.
Agents for the Applicants.