

[54] **TRICHLOROISOCYANURIC ACID  
STABILIZED WITH HYDRATED SODIUM  
DICHLOROISOCYANURATE**

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[21] Appl. No.: **356,350**

### Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 309,599, Nov. 24,  
1972, abandoned.

[52] U.S. Cl. .... **252/187 C; 8/108; 252/95**

[51] Int. Cl.<sup>2</sup>. **C11D 3/395; C11D 7/54; D06L 3/00**

[58] Field of Search ..... **252/187 C, 95, 98, 108;  
8/108**

### References Cited

#### UNITED STATES PATENTS

2,980,622 4/1961 Symes ..... 252/187 C

|           |        |                  |           |
|-----------|--------|------------------|-----------|
| 3,035,057 | 5/1962 | Symes .....      | 252/187 C |
| 3,178,372 | 4/1965 | Pomot .....      | 252/187 C |
| 3,397,206 | 8/1968 | Nicolaisen ..... | 252/187 C |

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### [57] ABSTRACT

A chlorine dry bleach having as its essential components trichloroisocyanuric acid and as a chemical stabilizer therefor hydrated sodium dichloroisocyanurate the water content of which is from about 7 to about 14%. The composition has excellent storage properties and generally good thermal stability and exhibits higher water solubility than trichloroisocyanuric acid alone. It can be used in any application calling for a source of active chlorine such as in water supplies for preventing the growth of pathogenic bacteria or as a bleach in detergents and as a sanitizing agent.

**3 Claims, No Drawings**

# TRICHLOROISOCYANURIC ACID STABILIZED WITH HYDRATED SODIUM DICHLOROISOCYANURATE

## CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of Ser. No. 309,599, filed Nov. 24, 1972, and now abandoned.

This invention relates to chlorinated isocyanurates, particularly to blends of hydrated sodium dichloroisocyanurate and trichloroisocyanuric acid.

The chlorinated cyanuric acids and their salts are well known as a source of active chlorine and are widely used in water supplies to prevent the growth of pathogenic bacteria in swimming pools and in detergent and sanitizing compositions. Of all the chlorinated isocyanurates, trichloroisocyanuric acid has the highest chlorine content and accordingly is often the preferred member of the series. However, trichloroisocyanuric acid is susceptible to a peculiar type of chemical instability as manifested by the evolution of noxious nitrogen trichloride fumes in the event the material remains in contact with air. It is generally conceded that moisture in the air is the causative factor in the breakdown since the effect is less severe under desiccated conditions.

It is known that the storage properties of trichloroisocyanuric acid can be improved by the addition thereto of certain stabilizing substances and in this connection reference is made to U.S. Pat. No. 3,278,443 on the use of olefins; British Pat. No. 1,197,689 on the use of sulfamates; and U.S. Pat. No. 3,342,684 on the use of metal carboxylates. Although generally satisfactory, such additives are objectionable in so far as they act as diluents and thereby cut down on the available chlorine of the stabilized trichloroisocyanuric acid compositions. A chemical complex of trichloroisocyanuric acid with potassium dichloroisocyanurate in the mole ratio of 1 to 4 of the type described in U.S. Pat. No. 3,275,630 and which is a well known commercial dry bleach, while superior in storage properties to the free acid, is objectionable in that it undergoes self-sustaining, thermally initiated decomposition. The same applies generally to physical mixtures of trichloroisocyanuric acid and alkali metal dichloroisocyanurates.

It has now been discovered that the chemical decomposition of trichloroisocyanuric acid can be greatly minimized without substantial sacrifice of available chlorine by blending the trichloroisocyanuric acid with an effective amount of hydrated sodium dichloroisocyanurate containing from about 7 to about 14% by weight of water of hydration. Considering the fact that moisture normally accelerates the chemical decomposition of trichloroisocyanuric acid, it is indeed most surprising that a hydrated salt with its relatively high water content would act as a chemical stabilizer. Moreover the water solubility of the mixture is higher than that of the unstabilized trichloroisocyanuric acid and this constitutes another unexpected and beneficial property of such compositions. Where the hydrated sodium dichloroisocyanurate is the dihydrate, the compositions are not subject to self-sustaining thermally initiated decomposition.

In carrying out the invention the trichloroisocyanuric acid and hydrated sodium dichloroisocyanurate are blended together in the usual manner of mixing solid

materials. Suitable mixing devices include rotating trays, ribbon blenders, tumblers or other low energy comminuting equipment. The mixture may also be compacted under pressure and then ground to the desired particle size for maximum homogeneity.

The proportion of the two components may vary considerably. For instance, only a small amount of the hydrated sodium dichloroisocyanurate is required to chemically stabilize the trichloroisocyanuric acid. In general, satisfactory results can be achieved wherein the mixture contains any amount in excess of about 1% by weight of the hydrated salt.

As previously pointed out, in addition to their chemical stability, the compositions of the invention possess greater water solubility than trichloroisocyanuric acid alone, the solubility of the mixture rising as the quantity of hydrated sodium dichloroisocyanurate is increased. Accordingly, the upper range of the hydrate will tend to be a compromise between solubility and chlorine content of the mixture. Thus, in the event high chlorine content is desired that will require a greater quantity of trichloroisocyanuric acid with concomitant lower solubility. If on the other hand, high solubility is required then more of the hydrate will be needed at the expense of available chlorine. Those skilled in the art will select the ratio of trichloroisocyanuric acid to hydrated sodium dichloroisocyanurate best suited to their particular needs.

As understood herein, the term hydrated sodium dichloroisocyanurate encompasses sodium dichloroisocyanurate monohydrate, having a water of crystallization content of 7% and sodium dichloroisocyanurate dihydrate having a water of crystallization content of 14% as well as mixtures of the two hydrates.

In addition to their enhanced solubility and resistance to breakdown during storage, the chemically stabilized trichloroisocyanuric acid compositions of the invention are thermally stable. That is to say, the compositions are not subject to the self-sustaining, thermally initiated decomposition peculiar to anhydrous sodium dichloroisocyanurate, the active agent in many dry bleach formulations which are sold commercially. Such thermal stability is exhibited in any ratio of trichloroisocyanuric acid to sodium dichloroisocyanurate dihydrate. Compositions herein containing up to about 90% by weight of sodium dichloroisocyanurate monohydrate are likewise thermally stable as above described. The latter is rather unusual and unexpected since the monohydrate itself undergoes self-sustaining, thermally initiated decomposition. In other words, a mere 10% or so of trichloroisocyanuric acid suffices to arrest the thermal breakdown of sodium dichloroisocyanurate monohydrate and to produce a chemically and thermally stable composition.

Reference is made to the following non-limiting examples.

## EXAMPLE 1

A 500 ml Patterson-Kelly Twin Shell Blender was charged with 300 gms of sodium dichloroisocyanurate dihydrate (-20+70 mesh) and 100 gms of trichloroisocyanuric acid (-20+70 mesh) and blended for 15 minutes. The resultant product was a granular, free-flowing material which assayed 64.0% available chlorine (theory 64.0%).

Two hundred and fifty grams of the product was stored in a sealed container at 130°F for 8 days. Upon completion of the test, the product was odorless, free-

flowing with no evidence of any chemical decomposition. The product assayed 63.9% available chlorine.

#### EXAMPLE 2

Various concentrations of sodium dichloroisocyanurate dihydrate/trichloroisocyanuric acid blends were tested for progressive, thermally initiated decomposition. An 18 gage nichrome wire was embedded in a 25 gram sample. The wire was heated by passing a current through it for several seconds, until the material in contact with the wire decomposed. The current was turned off and the decomposition was observed to determine the tendency for self-propagation.

The results of the tests at various concentration levels are listed in Table I.

TABLE I

| Sodium Dichloroisocyanurate Dihydrate<br>Trichloroisocyanuric Acid<br>Composition<br>Weight % | Decomposition |
|---|---------------|
| 100/0   | incomplete*   |
| 90/10   | incomplete    |
| 80/20   | incomplete    |
| 75/25   | incomplete**  |
| 65/35   | incomplete    |
| 50/50   | incomplete    |
| 25/75   | incomplete    |
| 20/80   | incomplete    |
| 10/90   | incomplete    |
| 5/95  | incomplete    |
| 0/100   | incomplete    |

\*Incomplete since the decomposition stopped after the current was shut off with major amounts of undecomposed material remaining.

\*\*Sample of this mix after prolonged thermal test was also incomplete

As will be noted, none of the sodium dichloroisocyanurate dihydrate/trichloroisocyanuric acid formulations listed in Table I exhibit progressive, thermally initiated decomposition. Such mixtures are both thermally and chemically stable.

#### EXAMPLE 3

In this example, the compositions of the invention were compared to blends of various chlorinated isocyanurates with respect to progressive, thermally initiated decomposition in accordance with the procedure of Example 2. The results are listed in Table II.

TABLE II

| Sample  | Composition<br>Weight % | Decomposition                    |
|---|-------------------------|----------------------------------|
| <b>Chlorinated Isocyanurate Compositions of Prior Art</b>             |                         |                                  |
| 1. Sodium dichloroisocyanurate anhydrous/trichloroisocyanuric acid    | 80/20                   | complete and rapid decomposition |
| 2. Sodium dichloroisocyanurate anhydrous/trichloroisocyanuric acid    | 65/35                   | complete and rapid decomposition |
| 3. Potassium dichloroisocyanurate anhydrous/trichloroisocyanuric acid | 80/20                   | complete and rapid decomposition |
| 4. Potassium dichloroisocyanurate anhydrous/trichloroisocyanuric acid | 65/35                   | complete and rapid decomposition |
| <b>Chlorinated Isocyanurate Compositions of Invention</b>             |                         |                                  |
| 5. Sodium dichloroisocyanurate dihydrate/trichloroisocyanuric acid    | 80/20                   | incomplete                       |
| 6. Sodium dichloroisocyanurate dihydrate/trichloroisocyanuric acid    | 65/35                   | incomplete                       |

#### EXAMPLE 4

Samples listed in Table III were prepared containing by weight 80% of the specified blends of chlorinated isocyanurates and 20% by weight of selected grade red oak sawdust following the proposed Bureau of Mines procedure RI 7594. In addition a control sample was prepared with pure sawdust. Each sample was placed in a bed 1×2×7 inches long and ignited with a flame and rate of burning was timed. The results are listed in Table III.

TABLE III

| Chlorinated Isocyanurate Blends                                       | Proportions of Blend<br>Weight % | Burning Rate<br>In./Min. |
|---|----------------------------------|--------------------------|
| 1. Sawdust (control)  | —                                | 3.1                      |
| Chlorinated Isocyanurate Composition of Invention                     |                                  |                          |
| 2. Sodium dichloroisocyanurate dihydrate/trichloroisocyanuric acid    | 75/25                            | 2.1                      |
| Chlorinated Isocyanurate Compositions of Prior Art                    |                                  |                          |
| 3. Sodium dichloroisocyanurate anhydrous/trichloroisocyanuric acid    | 75/25                            | 6.7                      |
| 4. Potassium dichloroisocyanurate anhydrous/trichloroisocyanuric acid | 75/25                            | 6.0                      |

As is evident from the test results in Table III, the flammability of fuel materials in contact with the thermally stable composition of the invention (sample 2) is one-third that of corresponding anhydrous mixtures.

#### EXAMPLE 5

Various concentrations of sodium dichloroisocyanurate monohydrate/trichloroisocyanuric acid blends were tested for progressive thermally initiated decomposition in the same manner as described in Example 2. Blends containing 90% or less of the monohydrate did not exhibit thermal decomposition.

The results of these tests are listed in Table IV.

TABLE IV

| Sodium Dichloroisocyanurate monohydrate/<br>trichloroisocyanuric Acid<br>Composition<br>Weight % | Decomposition                       |
|--|-------------------------------------|
| 100/0  | Complete and rapid<br>decomposition |
| 95/5   | Complete and rapid<br>decomposition |
| 90/10  | Incomplete                          |
| 75/25  | Incomplete                          |
| 50/50  | Incomplete                          |
| 25/75  | Incomplete                          |
| 10/90  | Incomplete                          |
| 5/95   | Incomplete                          |
| 0/100  | Incomplete                          |

EXAMPLE 6

The purpose of this example is to demonstrate the chemical stability of chlorinated isocyanurates in terms of their relative propensity to release nitrogen trichloride when subjected to a controlled moisture test. The test procedure was carried out as follows:

5 and 10 g quantities of the test specimen were each slurried in 50 ml of carbon tetrachloride. Samples of the solution were withdrawn after about 5 minutes and analyzed for the presence of nitrogen trichloride by means of UV absorbtion against a UV standard for ni-

trogen trichloride. 20 and 40 ml of water were added respectively to the 5 thoroughly 10 g slurries and each thoroughly shaken. Samples of the carbon tetrachloride solution were removed at about 5 minute intervals, then subjected to UV analysis to determine the amount of nitrogen trichloride therein. About four such sam-

5 ples were taken at five minute intervals and so tested. Based on the test procedure aforesaid a mixture of 75% by weight sodium dichloroisocyanurate and 25% 10 by weight trichloroisocyanuric acid exhibited much higher chemical stability than trichloroisocyanuric acid alone.

Other compositions containing trichloroisocyanuric acid and sodium dichloroisocyanurate exhibited com- 15 parable stability.

What is claimed is:

1. A chlorine dry bleach containing as its essential in- 20 gredients trichloroisocyanuric acid and hydrates of sodium dichloroisocyanurate as a chemical stabilizer therefor at least about 1% by weight of the composition.

2. A composition according to claim 1 wherein the chemical stabilizer is sodium dichloroisocyanurate 25 monohydrate.

3. A composition according to claim 1 wherein the chemical stabilizer is sodium dichloroisocyanurate di- hydrate.

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**UNITED STATES PATENT OFFICE**  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 3,919,103  
DATED : November 11, 1975  
INVENTOR(S) : SIDNEY BERKOWITZ

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 34, "3,342,684" should read --3,342,674--.

Column 2, line 21, "that" should read --this--.

Column 3, line 17 (Table I), "Dihydrate" should --Dihydrate/--.

Column 6, line 2, "5 thoroughly 10" should read --5 and 10g slurries and each thoroughly shaken.--

**Signed and Sealed this**  
*twenty-second Day of June 1976*

[SEAL]

*Attest:*

**RUTH C. MASON**  
*Attesting Officer*

**C. MARSHALL DANN**  
*Commissioner of Patents and Trademarks*