

[54] THERMALLY STABLE NITROSTARCH
[75] Inventor: Joseph S. Stack, Riverdale, N.J.
[73] Assignee: The United States of America as
represented by the Secretary of the
Army, Washington, D.C.
[22] Filed: Nov. 23, 1966
[21] Appl. No.: 596,737
[52] U.S. Cl. 149/108; 260/235
[51] Int. Cl. C06b 9/04
[58] Field of Search 149/108, 58, 19; 260/235;
23/75

[56]	References Cited		
	UNITED STATES PATENTS		
3,050,423	8/1962	Hudson	149/19
3,086,895	4/1963	Schaeffer et al.	149/19
3,092,527	6/1963	Schaafsma	149/19
3,109,761	11/1963	Cobb et al.	149/19
3,117,898	1/1964	Hedrick et al.	149/19
3,131,100	4/1964	Ratliff et al.	149/19
3,132,976	5/1964	Klager et al.	149/19
3,145,192	8/1964	Perry et al.	149/19 X

3,157,025 11/1964 Herring et al. 149/19 X
3,245,849 4/1966 Klager et al. 149/19
3,256,214 6/1966 Bluhm 149/19 |

Primary Examiner—Stephen J. Lechert, Jr.
Attorney, Agent, or Firm—Nathan Edelberg; Robert P. Gibson; A. Victor Erkkila

EXEMPLARY CLAIM

1. A urethane complex consisting of the reaction product of nitrostarch and an isocyanate selected from the group consisting of
2,4-tolylene diisocyanate,
4,4'-diphenylmethane diisocyanate,
1,5-napthalene diisocyanate,
p-tolylene isocyanate,
3,3'-dimethoxy-4,4'-biphenyl diisocyanate,
3,3'-dimethyl-4,4'-biphenyl diisocyanate,
phenylene diisocyanate
hexamethylene diisocyanate, and
heptamethylene diisocyanate,
said complex having thermal stability above 65°C for use in munitions.

12 Claims, No Drawings

THERMALLY STABLE NITROSTARCH

This invention relates to a modified form of nitrostarch having improved properties with respect to thermal stability.

The only high energy polymeric binder currently being employed in conventional propellants is nitrocellulose. The attractiveness of nitrocellulose for use in propellants is based on favorable physical characteristics, chemical and thermal stability, and thermo-chemical properties. The physical characteristics of nitrocellulose are such that it can be gelatinized with common solvents to form reasonably tough colloids, which is a necessary characteristic of binders for propellants. Further, nitrocellulose is chemically and thermally stable at normal to somewhat higher than normal temperatures. Also, nitrocellulose is oxygen sufficient and has a heat of explosion of 940 to 1,140 calories per gram depending upon the nitrogen content. As a result of these features, nitrocellulose has been found to be quite acceptable for use in munitions. However, on the other hand, it is quite advisable for the government to have a broad base of acceptable substitutes for the proven and accepted ingredients of today's munitions such as the conventional binder specified above and the like. But, to date, all efforts to find a polymeric binder for propellants with chemical, physical, thermal and thermo-chemical properties equivalent to nitrocellulose, which is also capable of being produced from cheap available starting material at a low cost, have been unsuccessful.

To date, of all known potential high energy polymeric binder material, nitrostarch most nearly exhibits properties comparable to nitrocellulose and may be manufactured at low cost from cheap available material. As is well known, nitrostarch is a mixture of nitrates obtained from nitrating conventional starch, of which sources are practically unlimited. For instance, such starch may be produced from corn, cassava and potatoes which are abundant. However, one of the major disadvantages of nitrostarch which prohibits its use as an explosive ingredient and potential binder in propellants is its relatively low thermal stability. It is common knowledge that nitrostarch is considerably less stable than nitrocellulose. For instance, nitrocellulose does not deflagrate after 5 hours exposure at 134.5°C whereas nitrostarch deflagrates in 65 minutes at 120°C. As such, nitrostarch in the past has been unacceptable as a substitute for nitrocellulose in munitions.

It is therefore an object of this invention to provide an acceptable substitute for nitrocellulose as a binder in propellants.

Another object is to provide a thermally stable form of nitrostarch, which is a substantial equivalent for nitrocellulose, as a binder for use in propellants.

A further object is to provide a chemically modified form of nitrostarch having physical, chemical and thermal properties which render it effective as a binder for propellants.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood from the following detailed description.

It has now been discovered that nitrostarch may be reacted with 2,4-tolylene diisocyanate to form a highly stable form of nitrostarch with respect to its thermal

properties. In theory, the product resulting from the above reaction may be a modified complex form of nitrostarch, such as a urethane of starch nitrate, and the reaction may be between the available hydroxyl groups on the nitrostarch and the isocyanate groups in 2,4-tolylene diisocyanate. In any case, the product formed is chemically and thermally acceptable as a substitute for nitrocellulose.

The following is an example of the procedure generally utilized to render nitrostarch more thermally stable:

EXAMPLE I

34 grams of dry nitrostarch are dissolved in 500 cc of acetone and 1.7 grams of 2,4-tolylene diisocyanate are added. The mass is intimately mixed, left standing for about 15 hours, and the resulting lacquer is then added dropwise to water accompanied by vigorous agitation. Sufficient water should be used so as not to permit resolution of the precipitated product. For instance, 500 cc of the lacquer solution are dropped into 2 liters of water. The precipitate which is formed is then filtered and dried at ambient temperature.

The example which follows illustrates the method of testing the material under study in order to specify the initial, intermediate, and final stages of thermal decomposition of the products set forth in Table 1 below.

EXAMPLE II

A dried specimen of approximately 2.5 grams of each of the materials to be tested is placed into an individual test tube and pressed to within 2 inches of the bottom of the tube. Drying of the sample may be initially accomplished on paper trays at a temperature between 38°C to 42°C. A piece of standardized methyl violet indicator paper is then placed in a vertical position in the tube such that the lower end of the indicator paper is 25mm from the specimen. A cork having a small hole is placed in each tube and the corked tubes are placed in a constant temperature reflux bath at the temperature specified. The tubes are checked at 5 minute intervals to ascertain if there has been any change in the character of the contents.

When the methyl violet indicator paper takes on a salmon pink appearance, the initial degradation of the material is taking place. When red fumes become visually evident, this indicates the visible formation of the oxides of nitrogen, which is the next stage in the degradation of the material under test. In sequence, the material should then explode indicating the time of complete decomposition of the material under study. This latter action is usually accompanied by an audible noise and/or flame.

Table 1 below sets forth the properties of nitrostarch, which has been modified in accordance with this invention, in comparison with those of a nitrostarch control, a nitrocellulose control, and nitrostarch which has been modified with two conventional but entirely different organic stabilizers.

TABLE I

Test	1. Control Nitrocellulose (12.6%N)	2. Control Nitrostarch (12.94%N)	3. Nitrostarch (12.55%N)	4. Conventionally Stabilized Nitrostarch (12.94%N)	5. Conventionally Stabilized Nitrostarch (12.94%N)
120°C Heat Test, min.					
Salmon Pink	90	—	165	40	85
Red Fumes	110	—	None	—	—
Explosion or Deflagration	300+	65	500+	180	210
134.5°C Heat Test, min.					
Salmon Pink	30-35	—	45	30	40
Red Fumes	35	—	80	30	45
Explosion or Deflagration	300+	15	500+	65	60
Heat of Explosion, cal/g	936	1015	917	Est. 1000	Est. 1000
Effect of Solvents					
Acetone	Colloids	Colloids	Colloids	Colloids	Colloids
Ether/Alcohol	Colloids	Colloids	Colloids	Colloids	Colloids

As shown, the nitrostarch control (2) is highly unstable when compared to the nitrocellulose control (1). In fact, at the temperature tested, the nitrocellulose control is at least 5 to 20 times more stable than the nitrostarch control. However, the sample of nitrostarch (3) which has been modified in accordance with this invention is at least 8 to 30 times more stable than the nitrostarch control and is at least as stable as the nitrocellulose control. This is clearly an achievement in view of the art which is exemplified by columns 4 and 5 wherein the conventionally modified starches are slightly more stable than the nitrostarch control and less stable than the nitrocellulose control. The nitrostarch of column 4 was modified with resorcinol and the nitrostarch of column 5 was modified with 2-nitrodiphenylamine. These modifiers are known in the art to be conventional stabilizers. Also, as indicated, the nitrostarch modified in accordance with this invention forms a colloid with the conventional solvents which is a prerequisite for its use as a binder in propellants. Further, as a follow-up to Table I, Table II below illustrates the range of concentration of 2,4-tolylene diisocyanate that may be used to treat the nitrostarch and the effect of change of concentration on the stability of the modified nitrostarch.

TABLE II

A*	Salmon Pink	134.5°C Heat Test, min. Red Fumes	Explosion or Deflagration
1	30	40	60
5	45	80	500+
10	60	100	500+
15	65	120	500+

*A - percent by weight of the isocyanate compound utilized to treat the nitrostarch.

As indicated above, the thermal stability of the modified nitrostarch is effected by the concentration of the isocyanate compound utilized in the procedure. As the concentration of the diisocyanate used to stabilize the nitrostarch is increased, the resistance to thermal degradation of the treated nitrostarch is highly improved. At lower concentrations of diisocyanate, of approximately 1 to 3% by weight, the product will not exhibit the degree of stability that is most desired. However, if higher concentrations of diisocyanate are used (about 9 to 15%), the energy or heat of explosion of the prod-

uct is decreased. At a concentration of about 4 to 8% of diisocyanate, the procedure produces a product which exhibits the best degree of properties with respect to thermal stability and energy.

Although the procedure is described with particular reference to 2,4-tolylene diisocyanate, there are many other types of isocyanate which may be used to treat nitrostarch with comparable results to that shown in Tables I and II. For instance, aromatic isocyanates may be utilized in the procedure including such materials as 4,4'-diphenylmethane diisocyanate; 1,5-naphthalene diisocyanate; p-tolylene isocyanate; 3,3'-dimethyl - 4,4'-biphenyl diisocyanate, phenylene diisocyanate, and 3,3'-dimethoxy - 4,4'-biphenyl diisocyanate. These all will react with the available hydroxy groups on the nitrostarch to form a thermally stabilized product which will be acceptable as a substitute for nitrocellulose. In addition, isomers of the above isocyanates may also be effectively used to stabilize nitrostarch. Further, the stability of the nitrostarch, when treated with an aliphatic diisocyanate, would be comparable to that obtained with 2,4-tolylene diisocyanate. In general, aliphatic isocyanates with carbons ranging from C₁ to C₁₀ may be employed to stabilize nitrostarch including hexamethylene diisocyanate and heptamethylene diisocyanate.

Obviously, many modifications and variations of the present invention are possible in light of the above teaching. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A urethane complex consisting of the reaction product of nitrostarch and an isocyanate selected from the group consisting of
 - 2,4-tolylene diisocyanate,
 - 4,4'-diphenylmethane diisocyanate,
 - 1,5-naphthalene diisocyanate,
 - p-tolylene isocyanate,
 - 3,3'-dimethoxy - 4,4'-biphenyl diisocyanate,
 - 3,3'-dimethyl - 4,4'-biphenyl diisocyanate,
 - phenylene diisocyanate
 - hexamethylene diisocyanate, and
 - heptamethylene diisocyanate,
 said complex having thermal stability above 65°C for use in munitions.

5

2. The complex of claim 1 wherein said isocyanate is present in an amount between about 1 and 15 percent by weight based on the weight of said nitrostarch.

3. The complex of claim 1 wherein said isocyanate is present in an amount between 4 and 8 percent by weight based on the weight of said nitrostarch.

4. A urethane complex consisting of the reaction product of nitrostarch and 2,4-tolylene diisocyanate, said complex having thermal stability above 65°C for use in munitions.

5. A urethane complex consisting of the reaction product of nitrostarch and 4,4'-diphenylmethane diisocyanate, said complex having thermal stability above 65°C for use in munitions.

6. A urethane complex consisting of the reaction product of nitrostarch and 1,5-naphthalene diisocyanate, said complex having thermal stability above 65°C for use in munitions.

7. A urethane complex consisting of the reaction product of nitrostarch and p-tolylene isocyanate, said complex having thermal stability above 65°C for use in munitions.

6

8. A urethane complex consisting of the reaction product of nitrostarch and 3,3'-dimethoxy - 4,4'-biphenyl diisocyanate, said complex having thermal stability above 65°C for use in munitions.

9. A urethane complex consisting of the reaction product of nitrostarch and 3,3'-dimethyl - 4,4'-biphenyl diisocyanate, said complex having thermal stability above 65°C for use in munitions.

10. A urethane complex consisting of the reaction product of nitrostarch and phenylene diisocyanate, said complex having thermal stability above 65°C for use in munitions.

11. A urethane complex consisting of the reaction product of nitrostarch and hexamethylene diisocyanate, said complex having thermal stability above 65°C for use in munitions.

12. A urethane complex consisting of the reaction product of nitrostarch and heptamethylene diisocyanate, said complex having thermal stability above 65°C for use in munitions.

* * * * *

25

30

35

40

45

50

55

60

65