UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING HEXANITRODIPHENYLAMIN.

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To all whom it may concern:

Be it known that I, JOHN MARSHALL, of Swarthmore, in the county of Delaware, and in the State of Pennsylvania, have invented a certain new and useful Improvement in Processes of Making Hexanitrodiphenylamin, and do hereby declare that the following is a full, clear, and exact description thereof.

My invention relates particularly to the production of symmetrical 2.4.6.2^1.4^1.6^1-hexanitrodiphenylamin in an advantageous manner.

Previously symmetrical hexanitrodiphenylamin has been prepared by the nitration of 2.4-dinitrodiphenylamin with nitric acid of approximately 50% strength to form 2.4.2^1.4^1-tetranitrodiphenylamin, and then by the nitration of the tetranitrodiphenylamin with nitric acid of 90% strength to form symmetrical hexanitrodiphenylamin. It has previously been considered to be impossible to carry out the nitration of dinitrodiphenylamin to form hexanitrodiphenylamin with mixed nitric and sulfuric acids as is shown for instance by the statement to this effect in *Nitrosprengstoffe*, by Escales, p. 187, and also in *Z. Ges Scheiss und Spreng.* (1913) p. 205, and the above described wasteful method by using nitric acid without sulfuric acid has therefore been found to be necessary in the production of this compound. Furthermore, owing to the strength of the nitric acid used it was necessary to use a lead lined or enameled vessel to resist the action of the acid.

The object of my invention is to provide a process by means of which mixed nitric and sulfuric acids may be used to produce symmetrical hexanitrodiphenylamin, and with such strengths of acids that ordinary iron vessels may be used instead of lead lined or enameled vessels.

While my invention is capable of being carried out in many different ways, for the purpose of illustration I shall describe only one way of carrying out the same hereinafter.

For example—I prepare 2.4.6.2^1.4^1.6^1-hexanitrodiphenylamin in an iron water-jacketed vessel, provided with an agitator by introducing into the same with constant agitation, one part by weight of 2.4-dinitrodiphenylamin at a temperature of about 70° C., together with five parts by weight of mixed acid containing approximately 30% nitric acid, 55% sulfuric acid, and 15% water. Thereafter the temperature is raised to from 80 to 90° C., in any suitable manner, and the agitation is continued at this temperature for approximately one hour. Thereupon the mixture is cooled to 30° C., and the solid 2.4.2^1.4^1-tetranitrodiphenylamin is separated from the spent acid by filtration. The material thus obtained, in an acid condition, is added at 70° C., to five parts by weight of mixed acids containing 20% nitric acid, 75% to 80% sulfuric acid and 5% to 0% water in the vessel previously referred to. The mixture is then raised to 80 to 90° C., and kept at this temperature for from one to two hours. Thereafter the solid 2.4.6.2^1.4^1.6^1-hexanitrodiphenylamin is separated from the spent acid by filtration, is drowned in water, and washed with hot water until freed from acid. Afterward it is centrifuged from the wash water and dried.

While I have described my invention above in detail, I wish it to be understood that many changes may be made therein without departing from the spirit of the same.

I claim:—

1. The process which comprises treating 2.4-dinitrodiphenylamin at an elevated temperature with mixed nitric and sulfuric acids until a substantial proportion of said dinitrodiphenylamin has been converted into 2.4.2^1.4^1-tetranitrodiphenylamin.

2. The process which comprises treating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2^1.4^1-tetranitrodiphenylamin, and then further nitrating the resulting tetranitrodiphenylamin with mixed nitric and sulfuric acids.

3. The process which comprises nitrating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2^1.4^1-tetranitrodiphenylamin, and then treating the resulting tetranitrodiphenylamin at an elevated temperature with mixed nitric and sulfuric acids to form 2.4.6.2^1.4^1.6^1-hexanitrodiphenylamin.

4. The process of nitrating 2.4-dinitrodiphenylamin which comprises treating said dinitrodiphenylamin with mixed nitric and sulfuric acids, the strength of the acids used being such that they do not attack iron.

5. The process which comprises treating

2.4-dinitrodiphenylamin at an elevated temperature with mixed nitric and sulfuric acids under conditions so regulated as to form tetranitrodiphenylamin, the strength of the acids used being such that they do not attack iron.

6. The process which comprises treating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2¹.4¹-tetranitrodiphenylamin, and then further nitrating the resulting tetranitrodiphenylamin with mixed nitric and sulfuric acids, the strength of the acids used being such that they do not attack iron.

7. The process which comprises treating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2¹.4¹-tetranitrodiphenylamin, and then further nitrating the tetranitrodiphenylamin at an elevated temperature with mixed nitric and sulfuric acids to form 2.4.6.2¹.4¹.6¹-hexanitrodiphenylamin, the strength of the acids used being such that they do not attack iron.

8. The process which comprises nitrating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2¹.4¹-tetranitrodiphenylamin, and then further nitrating the tetranitrodiphenylamin with mixed nitric and sulfuric acids, the mixed acids containing in the first nitration 30% nitric acid and in the second nitration 20% nitric acid.

9. The process which comprises treating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids under conditions so regulated as to form 2.4.2¹.4¹-tetranitrodiphenylamin, and then nitrating the tetranitrodiphenylamin at an elevated temperature with mixed nitric and sulfuric acids to form 2.4.6.2¹.4¹.6¹ - hexanitrodiphenylamin, the mixed acids containing in the first nitration 30% nitric acid and in the second nitration 20% nitric acid.

10. The process which comprises treating dinitrodiphenylamin with mixed nitric and sulfuric acids, the treatment being carried out at from 80 to 90° C.

11. The process which comprises treating 2.4-dinitrodiphenylamin with mixed nitric and sulfuric acids to form 2.4.2¹.4¹-tetranitrodiphenylamin, the nitration being carried out at from 80 to 90° C.

12. The process which comprises treating 2.4.2¹.4¹-tetranitrodiphenylamin with mixed nitric and sulfuric acids, the nitration being carried out at from 80 to 90° C.

13. The process which comprises treating 2.4.2¹.4¹-tetranitrodiphenylamin with mixed nitric and sulfuric acids containing about 20% nitric acid under conditions so regulated as to form hexanitrodiphenylamin.

In testimony that I claim the foregoing I have hereunto set my hand.

JOHN MARSHALL.

Witnesses:
LYMAN L. TITUS,
GEO. H. GREGG.