# United States Patent

**Syrop**

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[54] **PROCESS FOR RECRYSTALLIZING HEXANITROSTILBENE**


[72] Inventor: **Leroy J. Syrop**, Sepulveda, Calif.

[73] Assignee: **Del Mar Engineering Laboratories**, Los Angeles, Calif.



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[52] **U.S. Cl.** .....**260/645**, 23/273, 149/105, 260/707

[51] **Int. Cl.**.....**C07c 79/10**

[58] **Field of Search**.....260/645



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*Primary Examiner*—Leland A. Sebastian
*Attorney*—Jessup & Beecher

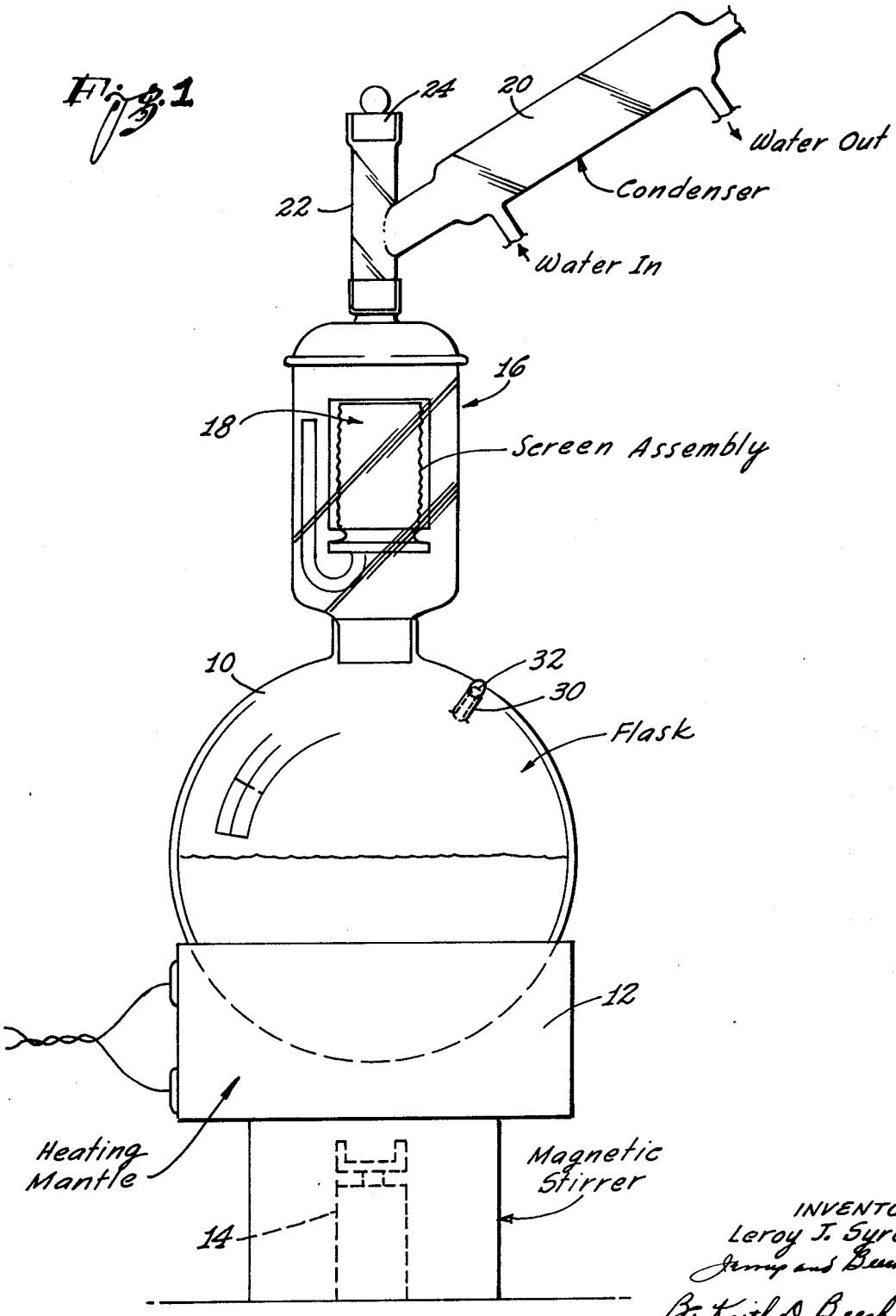


[57] **ABSTRACT**

An improved apparatus and process is provided for processing the explosive known as Hexanitrostilbene (HNS) from a form known as HNS-I into a form known as HNS-II, to provide a refined product with a unique crystal form so as to facilitate handling of the material. The process of the invention involves an improved extraction technique involving the use of a solution of acetonitrile in which HNS-I is soluble and xylene in which HNS is insoluble for refining the HNS-I into an improved type of HNS-II.


**6 Claims, 3 Drawing Figures**

Fig. 1




INVENTOR:
Leroy J. Syrop
Jenny and Bressler
By Keith D. Bressler
ATTORNEYS

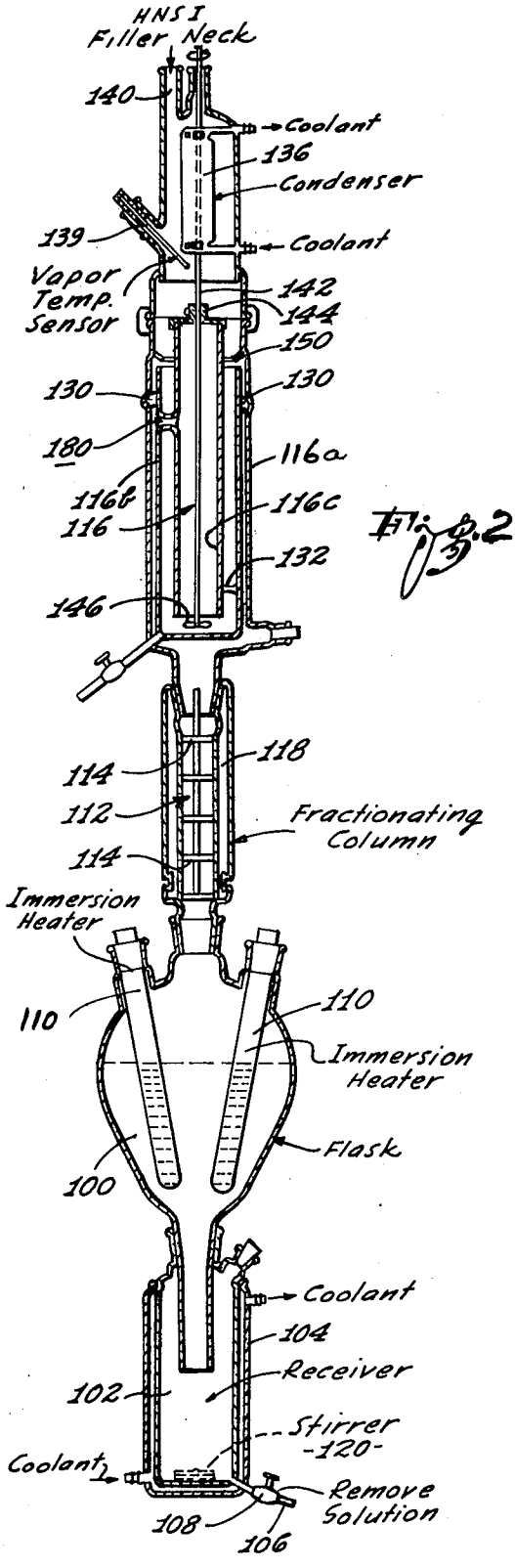



Fig. 2

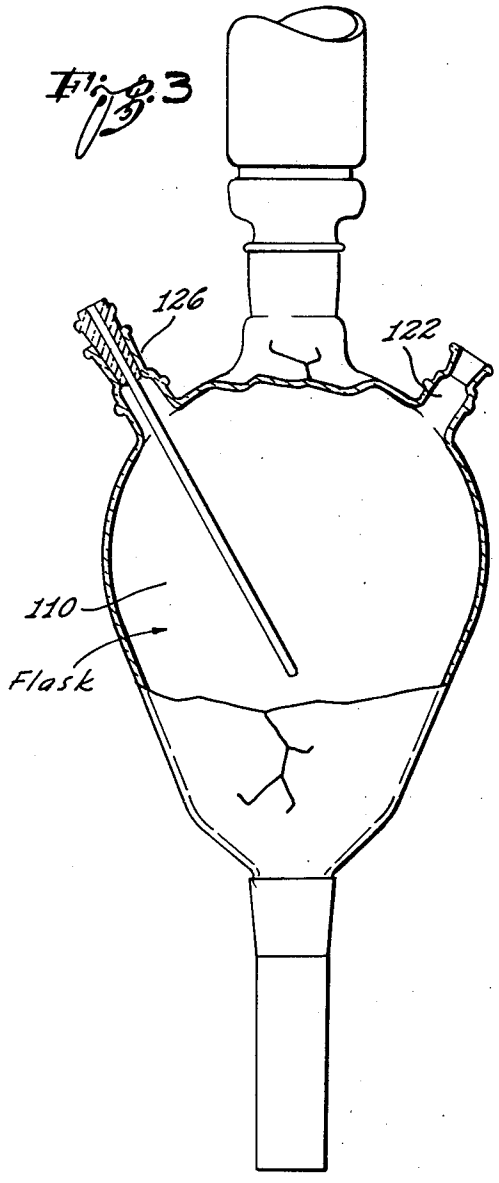



Fig. 3

INVENTOR
Leroy J. Syrop
Jenner and Boucher
By Keith D. Boucher
ATTORNEYS

# PROCESS FOR RECRYSTALLIZING HEXANITROSTILBENE

## BACKGROUND OF THE INVENTION

Hexanitrostilbene (HNS) was first produced at the Naval Ordnance Laboratory to meet a requirement for a heat resistant explosive. Subsequent research revealed that HNS possesses other properties which are superior to similar types of explosives and which have resulted in HNS being used for more general applications, even where heat resistance is not a critical factor.

Among the desirable features of HNS is the fact that it demonstrates acceptable performance in a temperature range extending, for example, from −320° to +325° C. which attests to the heat resistance properties of the material. In addition, HNS has been found to be relatively insensitive to electrostatic discharge, to be less sensitive to impact than tetryl, and to be radiation resistant. All the foregoing properties have led to the general acceptance of HNS as a superior material for explosive purposes.

The process and apparatus of the present invention are intended to produce on an efficient and high yield commercial scale large quantities of HNS-II from HNS-I by an improved recrystalization process. The HNS-II produced by the process and apparatus of the invention has controllable and predictable bulk densities of, for example, 0.5 to 1.0 grams per cubic centimeter. The process produces at the higher densities an extremely pure and free-flowing crystalline HNS-II material having a unique grain structure.

The free-flowing from of HNS-II produced by the process and apparatus of the invention is especially suited for use in automatic loading equipment. For example, the unique crystal form of the HNS-II produced by the process and apparatus of the invention enables it conveniently to be loaded into small diameter cord. The material has a denser, coarser and larger crystal than the HNS-II produced by the prior art methods, and has crystals of uniform shape and of a generally orthorombic configuration.

Basically, the process of the present invention serves to transform HNS-I into an improved form of HNS-II in which the crystal shape is changed, as mentioned above, so as to improve the handling characteristics of the resulting material. However, the HNS-II produced by the process of the invention also has certain ancillary features in that it is purer than the original HNS-I and can be compressed to a denser mass per unit volume so as to provide a more powerful explosive and one with different sensitivity to detonation, as compared with the original HNS-I.

In a prior art process for converting HNS-I into HNS-II, an extraction method was used involving acetonitrile which is a solvent insofar as HNS-I is concerned, and toluene which is a non-solvent to HNS-I. In the practice of the prior art process, both the liquid acetonitrile and the liquid toluene are placed in a flask and the flask is heated. Since the boiling point of acetonitrile (81° C) is lower than the boiling point of toluene (110° C), the acetonitrile boils first. The resulting acetonitrile vapor is caused to pass up to a condenser, and the condensed acetronitrile is passed through a quantity of HNS-I. The resulting solution of HNS-I, dissolved in the acetonitrile condensate, passes down into the flask, in which the toluene causes HNS-II to precipitate out of the solution. The aforesaid prior art process continues until all the available HNS-I has been dissolved and precipitated out as HNS-II.



However, the prior art process described in the preceding paragraph has certain inherent drawbacks. In the first place, the boiling points of the acetonitrile and toluene are sufficiently close together so that an appreciable amount of toluene vapor is produced during the process and is condensed along with the acetonitrile vapor. Therefore, the condensate passing through the HNS-I contains substantial amounts of toluene which inhibits the dissolution of the HNS-I into the acetonitrile condensate.

The aforesaid condition is aggravated in the prior art process by the fact that toluene and acetonitrile form an azeotrope with a boiling point lower than either the acetonitrile or the toluene. The resulting azeotrope results in further significant amounts of toluene appearing in the resulting vapor and in the subsequent condensate.

The foregoing factors result in low efficiency in the prior art process such that it is incapable of providing significant yield of HNS-II, or of operating on an efficient or economically feasible commercial basis. The process of the present invention overcomes the deficiency of the prior art process by using a non-solvent in the extraction process which has a boiling point materially above the boiling point of the solvent, and one which will not form an azeotrope with the solvent.

In the embodiment of the process to be described herein, the xylene in either its ortho, meta, or para form, or mixtures of all three forms, is used in conjunction with acetonitrile, the xylene replacing the toluene. The xylene has an advantage over the toluene in that its boiling point is about 140° C which represents a substantial displacement above the boiling point of the acetonitrile; and also in that the xylene does not form an azeotrope with the acetonitrile.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of appropriate apparatus in which the process of the invention may be carried out;

FIG. 2 is a side sectional view of improved apparatus constructed in accordance with the present invention for carrying out the process of the invention; and

FIG. 3 is a fragmentary showing of one of the components of the apparatus of FIG. 2, rotated 45° about its vertical axis as compared with the showing in FIG. 2.

## DETAILED DESCRIPTION OF THE PROCESS AND APPARATUS OF THE INVENTION

In the practice of the process of the invention, liquid xylene in either its ortho, meta or para form, or mixtures of all three forms, and liquid acetonitrile are placed in a flask, and the flask is heated to the boiling point of the acetonitrile so as to vaporize the acetonitrile. The resulting acetonitrile vapor is subsequently condensed, and passed down through a quantity of HNS-I. The resulting solution of HNS-I is dissolved in the acetonitrile condensate is returned to the original flask to precipitate the HNS-II out of the solution. The process is continued until all of the available HNS-I has been dissolved and subsequently precipitated as HNS-II in the original flask.

One simple form of apparatus for carrying out the process of the invention is shown in FIG. 1. The apparatus shown in FIG. 1 includes, for example, a flask 10 which may be a 12 liter size. The flask 10 is supported in an appropriate heating mantle 12 which may be electrically energized. A magnetic stirrer is provided under the heating mantle and under the flask 10, to maintain the contents of the flask in an agitated condition. An extractor housing 16 is supported in the neck of the flask 10, the extractor housing surrounding an internal screen cup 18, and including a condenser 20 and a neck 22. A stopper 24 is inserted in the upper end of the neck 22.

In the practice of the process of the invention the screen cup 18 is placed in the extractor housing, as shown in FIG. 1. The flask 10 has a further neck 30 which is closed by a stopper 32. The screen cup is filled with HNS-I material through the neck 22 by removing the stopper 24. Then, in the practice of a specific example of the process of the invention, 50 grams HNS-II seed are placed in the flask 10 through the neck 30 by removing the stopper 32. Three liters of acetonitrile and 5 liters of xylene (either ortho, meta, or para, or mixtures thereof) are inserted into the flask 10 through the neck 30. The stopper 32 is then replaced. The magnetic stirrer 14 is activated, and a coolant, such as water is passed through the condenser 20. The heating mantle 12 is then energized, and observed until the system reaches steady state conditions.

The aforesaid process is continued for 12–30 hours, or until all the HNS-I in the cup 18 has been dissolved. The heating mantle 12 is then de-energized, and the solutions in the flask 10 allowed to cool to ambient temperatures. The magnetic stirrer 14 is activated during this interval, since it is important for vigorous stirring to continue throughout the entire cooling process.

The cooled solution may then be removed from the flask 10 through the neck 30 and filtered, for example, in a Buchner funnel. This results in a liberating of the HNS-II. The liberated HNS-II is washed thoroughly, for example, in acetone, and then filtered. The resulting product is placed in drying pans and permitted to dry at temperatures in excess, for example, 100° C for 8 hours. The resulting HNS-II is found to have all the characteristics described above, which provides for a pure product, and one which may more easily be handled than the original HNS-I.

Improved apparatus constructed in accordance with the invention is shown in FIGS. 2 and 3. As mentioned above, FIG. 2 is a side sectional view of the apparatus, and FIG. 3 is a view, partly in section, of the flask portion rotated 45° about its vertical axis, as compared with the view of FIG. 2.

The apparatus shown in FIGS. 2 circulated. 3 is supported by appropriate bracket means (not shown). The apparatus includes a flask 100 which may have a capacity, for example, of 22 liters. The flask 100 has an upper neck and lower neck. The lower neck of the flask is supported in the neck of a receiver 102. The receiver 102 is surrounded, for example, by a jacket 104 through which a suitable coolant, such as water is circulated An outlet line 106 is provided at the bottom of the receiver 102, and the solution in the receiver may be removed by opening an appropriate stop cock 108.

The solution in the flask 100 is heated by means, for example, of a plurality of immersion heaters 110 which are inserted into the flask through appropriate necks disposed around the upper portion thereof. In a constructed embodiment, four evenly spaced heaters 110 are used, each having a power capability of 2 kilowatts. The heaters used in the constructed embodiment are formed of quartz, with a diameter of 1–11/16 inches, and a length of 19 inches.

A fractionating column 112 is inserted into the upper neck of the flask 100. The fractionating column includes a plurality of perforated plates 114 which serve as condensing surfaces for any vapor of the unwanted xylene. This causes the xylene to condense, so that the fractionating column serves to inhibit the xylene vapor from rising into the extractor 116, the extractor being supported above the fractionating column 112. The fractionating column includes a silvered evacuated jacket 118, which serves to insulate the column thermally from the external ambient temperature.

An appropriate stirrer 120 is provided in the receiver 102, the stirrer 120 being operated, for example, by mechanical means inserted into the receiver, or by appropriate external magnetic means. Likewise, a stirrer may be inserted into the flask 100 through the neck 122 illustrated in FIG. 3. A temperature sensor 124 may be inserted into the flask 100, as shown in FIG. 3, through the neck 126.

In carrying out the process of the invention, and as described above, the acetonitrile and xylene are inserted into the flask 100, and the solutions fill the flask and also the receiver 102. Then, the solution in the flask 100 is heated by the immersion heaters 110 so as to vaporize the acetonitrile, and to cause the acetonitrile vapor to rise through the fractionating column 112 and up through the extractor 116. The xylene, which has a higher boiling point than the acetonitrile, and as described above, does not vaporize to any material extent within the flask 100, and any xylene vapor that is generated is condensed and returned to the flask by the fractionating column 112, so that no measurable amount of xylene vapor reaches the extractor 116.

The extractor 116 includes a series of concentric tubes. For example, the extractor includes a first tube 116*a* forming the outer wall of the extractor, and a second tube 116*b* is supported within the tube 116*a* by rod supports 130. A third inner tube 116*c* is supported coaxially within the tube 116*b*, by means, for example, of rod supports such as the support 132. A condenser 136 is supported above the extractor 116, and an appropriate coolant, such as water, is circulated through the condenser. A temperature sensor 139 extends into the condenser, as shown.

A first filler neck 140 is provided in the housing 138, and the HNS-I is continuously inserted into the housing through that filler neck. The HNS-I may be fed into the apparatus through the filler neck by appropriate automatic means, so that a predetermined amount of HNS-I is continuously fed into the system.

A rotatably driven stirrer rod 142 extends down through the housing 138 and down into the tube 116*c* of the extractor. The rod is supported, for example, in a Teflon bearing 144 at the upper end of the tube 116*c*. A stirrer 146 is mounted at the lower end of the rod

142, and between the open lower end of the tube **116***c* and the closed lower end of the tubular member **116***b*.

In the operation of the apparatus, the acetonitrile vapor from the fractionating column **118** rises into the extractor **116** and through the annular space between the tube **116***b* and the tube **116***a*. The vapor then rises into the housing **138** where it is condensed by the condenser **136**. The resulting condensate passes down into the extractor and over a drip ring **150**. The HNS-I inserted into the filler neck **140** is dissolved into the condensate in accordance with the practice of the process as described above.

The condensate and dissolved HNS-I passes down through the annular space between the tubes **116***c* and **116***b* to the bottom of the tube **116***b*. The accumulating liquid is then forced up into the interior of the tube **116***c* and through an overflow orifice **180** into the space between the tubes **116***a* and **116***b*, and down through the fractionating column **118** into the flask **100**. During this process, the stirrer **146** is turning in a direction so that its blades tend to force any solids in the liquid back up into the space between the tubes **116***b* and **116***c*, so that the HNS-I may be fully dissolved in the condensate as it overflows through the orifice **180** and down into the flask **100**.

The rate of feed of the HNS-I, and temperatures are controlled so that a continuous action is achieved, and so that the acetonitrile condensate saturated with HNS-I is received into the flask **100**. Appropriate filter means may be provided in the orifice **180**, to assure that no solid HNS-I passes down into the flask **100**.

Then, as in the previously described apparatus, the xylene in the flask **100** precipitates HNS-II out of solution, and the precipitated HNS-II passes down into the receiver **102** where it is cooled. The cooled solution may periodically be removed by opening the stop cock valve **108**, and filtering. Then, as before, the resulting HNS-II is placed in drying pans and permitted to dry at the predetermined temperatures.

The apparatus of FIG. **3** is advantageous in that it permits a continuous extraction process of HNS-II to be carried out, whereby the HNS-II is produced on a continuous and commercial basis within the receiver **102**. The process and apparatus of the invention operate efficiently to yield high grade HNS-II on an economical commercial basis.

Although particular embodiments of the process and apparatus of the invention have been described, modifications may be made. It is intended to cover all such modifications which fall within the scope of the invention in the following claims.

What is claimed is:

**1**. A process for recrystalizing hexanitrostilbene from a Type-I to a Type-II consistency, said process comprising: dissolving Type-I hexanitrostilbene in a selected solvent solution having a particular boiling point; and introducing the solvent and dissolved Type-I hexanitrostilbene into a precipitant solution having a boiling point displaced above the boiling point of said solvent solution and which is incapable of forming an azeotrope with said solvent.

**2**. The process defined in claim **1**, in which said boiling point of said precipitant solution is displaced substantially 60° C above the boiling point of said solvent solution.

**3**. The process defined in claim **1**, in which said solvent is acetronitrile.

**4**. The process defined in claim **3**, in which said precipitant is xylene.

**5**. The process defined in claim **4**, in which said xylene is of a type selected from a group consisting of ortho, meta and para xylene.

**6**. The process defined in claim **1**, in which said solvent solution and precipitant solution are initially mixed together, and in which said solvent is vaporized and condensed so that the condensate may pass through the aforesaid Type-I hexanitrostilbene and into the precipitant solution.

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