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(54) **Title:** PROCESS FOR PRODUCING DIALLYL DISULFIDE

(57) **Abstract:** The invention provides a process for forming diallyl disulfide. The process comprises A) mixing together sulfur and at least one alkali metal sulfide in an initial aqueous medium in which at least about 90 volume percent of said aqueous medium is water, such that a disulfide source is formed in said initial aqueous medium thereby forming a disulfide source-conatining aqueous medium, and B) mixing together at least a portion of said disulfide source-containing aqueous medium and at lease one allyl halide selected from allyl cloride, allyl bromide, or a mixture of any two or all three of these, in the absence of any additional solvent other than water, at a temperature in the range of about 40°C to about 60°C, such that diallyl disulfide is formed.

WO 2006/016881 A1

PROCESS FOR PRODUCING DIALLYL DISULFIDE

TECHNICAL FIELD

[0001] This invention relates to a process for producing diallyl disulfide from an allyl halide.

BACKGROUND

[0002] There are several known processes for production of diallyl disulfide. Some of these processes involve the synthesis of sodium disulfide from sodium sulfide and sulfur; the sodium disulfide is then reacted with allyl chloride or allyl bromide to make diallyl disulfide. See for example Hungarian Patent 166880 (publication number 09289; *Chem. Abstracts* 82:170041, 1975). However, a few of these processes require a phase transfer catalyst, a solvent in addition to water, or both. See in this connection Nosyreva and Amosova, *Russian J. Org. Chem. Engl. Translation*, 1990, 1218-1221, and Hase and Perakyla, *Synth. Comm.*, 1982, **12**, 947-950. A process that does not require a phase transfer catalyst or a non-aqueous solvent would be desirable. It would be a further advantage if such a process produced diallyl disulfide in good yield, especially while minimizing the production of unwanted byproducts.

SUMMARY OF INVENTION

[0003] A process according to the invention produces diallyl disulfide that meets U.S. Environmental Protection Agency registration standards. In addition to producing a product now approved for registration, processes of the invention minimize the formation of unwanted byproducts, and can be operated successfully in the absence of a phase-transfer catalyst, and do not require the use of non-aqueous solvent. High yield of diallyl disulfide is still another advantage of the processes of the present invention.

[0004] An embodiment of this invention is a process which comprises

A) mixing together sulfur and at least one alkali metal sulfide in an initial aqueous medium in which at least about 90 volume percent of said aqueous medium is water, such that a disulfide source is formed in said initial aqueous medium thereby forming a disulfide source-containing aqueous medium, and

B) mixing together at least a portion of said disulfide source-containing aqueous medium and at least one allyl halide selected from allyl chloride, allyl bromide, allyl iodide, or a mixture of any two or all three of these, in the absence of any

additional solvent other than water, at a temperature in the range of about 40°C to about 60°C,

such that diallyl disulfide is formed.

[0005] Another embodiment of this invention is a process which comprises mixing together a disulfide source-containing aqueous medium and at least one allyl halide selected from allyl chloride, allyl bromide, allyl iodide, or a mixture of any two or all three of these, in the absence of any additional solvent other than water, at a temperature in the range of about 40°C to about 60°C, such that diallyl disulfide is formed.

[0006] These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0007] The absence of oxygen is recommended and preferable in the processes of the invention due to the flammability of the allyl halide. Thus, the minimization of oxygen in manipulations involving allyl halides is recommended and preferred. It is preferred that such operations are conducted in an inert atmosphere comprised of one or more inert gases, such as, for example, nitrogen, helium, or argon. Nitrogen is a preferred inert gas.

[0008] It may be desirable, although it is not necessary, to add a small amount of a base or an aqueous basic solution, such as an alkali metal hydroxide solution, to the reaction zone. Keeping the reaction mass basic helps to prevent the formation of poisonous hydrogen sulfide, which can occur under acidic conditions, and also prevents damage from hydrohalic acid gas that might be released by unreacted allyl halide. Preferably, the basicity is provided by an alkali metal hydroxide solution, preferably sodium hydroxide or potassium hydroxide, more preferably sodium hydroxide.

[0009] Surprisingly, it has been found that the presence of one or more ancillary solvents is not necessary at any point in the processes of the invention; *i.e.*, no additional solvent is needed for the processes of the invention to work, where "ancillary solvent" refers herein to any solvent other than water. Thus, at least about 90 volume percent of said aqueous medium is water. Preferably, at least about 95 volume percent of the aqueous medium is water; more preferably, at least about 97.5 volume percent of the aqueous medium is water. Even more preferably, the only ancillary solvent(s) present in the aqueous medium are trace amounts that are adventitious, *i.e.*, at least about 99 volume percent of the

aqueous medium is water. Furthermore, the introduction of one or more other solvents can cause contamination of the reaction medium, and presents another flammability hazard. Water, from whatever source or sources, that makes up the aqueous medium should not and preferably does not contain ancillary solvent in such amount as to cause less than about 90 volume percent of the aqueous medium to be water. Thus, for example, water that becomes part of the aqueous medium from aqueous solutions of reagents should not contribute significant amounts of ancillary solvent, and preferably contributes little, if any, ancillary solvent to the aqueous medium.

[0010] In the practice of this invention, sulfur can be used in solid form, in molten form, or both. Suitable solid forms of sulfur include powder, granules, briquettes, and the like. Preferred solid forms of sulfur are granules and briquettes, because they avoid the dust explosion hazard presented by the use of powder. More preferably, sulfur is used in molten form; the reaction zone need not be kept at temperatures which maintain the sulfur in molten form.

[0011] The alkali metal sulfide can be lithium sulfide, sodium sulfide, potassium sulfide, rubidium sulfide, cesium sulfide, or a mixture of any two or more of these. Preferably, the alkali metal sulfide is lithium sulfide, sodium sulfide, or potassium sulfide, or a combination of any two or all three of these; more preferred are sodium sulfide and potassium sulfide, or a combination thereof. A particularly preferred alkali metal sulfide is sodium sulfide. The alkali metal sulfide can be in anhydrous form or in one or more of various hydrated forms. Because the alkali metal sulfide is to be mixed with water, anhydrous forms are considered unnecessary. Aqueous solutions of the alkali metal sulfide can also be used. Combinations of solid alkali metal sulfide and aqueous solution of alkali metal sulfide may be used (*e.g.*, when charged separately to the reaction zone). Since the water of the aqueous alkali metal sulfide solution normally becomes part of the aqueous medium, the solution should not have much ancillary solvent, if any, in the water.

[0012] The mole ratio of the sulfur to the alkali metal sulfide is preferably in the range of about 0.8:1 to about 1.2:1. More preferred is a ratio as near as practicable to 1:1, as the amount of sulfur relative to alkali metal sulfide affects the types of sulfur species (sulfide sources) produced in the aqueous medium. This in turn affects the product distribution observed when the disulfide source is mixed together with the allyl halide.

[0013] Standard methods for the feeding of solids, such as the use of hoppers, can be

used in the processes of the invention. A preferred method when feeding at least a portion of the sulfur and at least a portion of alkali metal sulfide as a solid is to mix the alkali metal sulfide with sulfur in the hopper. It has been observed that this method reduces or minimizes problems, such as bridging, which can occur during the feed of solids.

[0014] When sulfur is used in solid form, the aqueous medium usually should be heated to at least about 45°C and stirred at such temperature or temperatures for about an hour on the plant scale to disperse the sulfur in the aqueous medium. Preferably, the aqueous medium is heated to at least about 60°C. Once the sulfur has been dispersed, the reactor is usually cooled to the temperature at which the disulfide source and the allyl halide are mixed together. Heating to disperse the sulfur can be done before, during, or after mixing with the alkali metal sulfide.

[0015] Generally, the alkali metal sulfide needs to be dispersed or dissolved in the initial aqueous medium. The concentration of alkali metal sulfide in the initial aqueous medium is normally and preferably in the range of about 10 wt% to about 20 wt%. More preferably, the alkali metal sulfide concentration is in the range of about 15 wt% to about 20 wt%. Deviations from these concentration ranges are possible in the practice of this invention. However, the preferred ranges are recommended in order to keep the alkali metal sulfide, disulfide source, and the product alkali metal halide, which is coproduced with the diallyl disulfide, in the aqueous medium.

[0016] Formation of the disulfide source in the aqueous medium (or, a disulfide source-containing aqueous medium) is usually carried out at a temperature in the range of about 35°C to about 70°C. Of course, the temperature may vary within this range during the process. Preferably, temperatures in the range of about 40°C to about 65°C are used; more preferably, the temperature is in the range of about 45°C to about 60°C. It has been observed that increased temperature helps the alkali metal sulfide (when fed as a solid) and the sulfur to go into solution. Stirring times for the formation of the disulfide source on the plant scale are normally on the order of about half an hour to about three hours.

[0017] Without wishing to be bound by theory, it is generally believed in the art that an alkali metal disulfide is formed from the alkali metal sulfide and sulfur in the aqueous medium, according to the following equation:

$$A_2S + S \rightarrow A_2S_2$$

and diallyl disulfide is thought to be formed from the alkali metal disulfide according to the following equation:

$$A_2S_2 + 2 \text{ allyl halide} \rightarrow (\text{allyl})_2S_2 + 2 AX$$

where A is an alkali metal and X is chlorine, bromine, or iodine. If an alkali metal disulfide species is not formed, it is to be understood that the term alkali metal disulfide refers to whatever species are formed that react with allyl halides to form diallyl disulfide. Thus, the term "disulfide source" has been used throughout this document to indicate the species that react(s) with the allyl halide to form diallyl disulfide, whether the disulfide source is an alkali metal disulfide or one or more other species.

[0018] The allyl halide is allyl chloride, allyl bromide, allyl iodide, or a mixture of any two or all three of these. Allyl chloride and allyl bromide are preferred allyl halides; more preferred is allyl chloride.

[0019] The stoichiometric mole ratio of alkali metal disulfide (disulfide source) to allyl halide is 0.5:1; this is also a preferred stoichiometry at which to carry out the processes of the invention. It is possible to perform the processes of the invention with less than 0.5 moles of disulfide source per mole of allyl halide, but when so doing, the use of base is strongly recommended to prevent H_2S formation, which can occur under acidic conditions; precautions should also be taken to minimize hazards associated with excess allyl halide. Thus, the mole ratio of alkali metal disulfide to allyl halide is preferably at least about stoichiometric (0.5:1), or more preferably, the disulfide is used in excess relative to the allyl halide. It is preferred and recommended that the disulfide source is in excess relative to the allyl halide. To have the disulfide source in excess, the alkali metal sulfide is normally used in excess relative to the amount of allyl halide. This ensures that all of the allyl halide, which is reactive and toxic, is consumed. Preferably, the mole ratio of alkali metal disulfide to allyl halide is in the range of about 0.5:1 to about 0.875:1 (about 0% to about 75% excess disulfide). More preferred is a mole ratio in the range of about 0.5:1 to about 0.75:1 (about 0% to about 50% excess disulfide). Still more preferred is a mole ratio of alkali metal disulfide to allyl halide in the range of about 0.5:1 to about 0.62:1 (about 0% to about 25% excess disulfide). Even more preferred is a mole ratio in the range of about 0.5:1 to about 0.55:1 (about 0% to about 10% excess disulfide). A mole ratio of alkali metal disulfide to allyl halide in the range of about 0.5:1 to about 0.525:1 (about 0% to about 5% excess disulfide) is particularly preferred.

[0020] The mixing together of the allyl halide and the disulfide source-containing aqueous medium is carried out at a temperature in the range of about 40°C to about 60°C. Surprisingly, it has been found that the formation of undesired byproducts, such as monosulfides, trisulfides, and tetrasulfides, is minimized in favor of formation of diallyl disulfide in this temperature range. More preferably, the temperature is in the range of about 40°C to about 50°C; still more preferably, the temperature is in the range of about 45°C to about 50°C. Because the reaction of allyl halide and disulfide source is quite exothermic, it may be necessary to cool the reaction zone to maintain the temperature in the desired range.

[0021] A particularly preferred way of mixing together the allyl halide and the disulfide source-containing aqueous medium is to feed the allyl halide subsurface to the disulfide source-containing aqueous medium. Subsurface feeding allows for more efficient mixing of the allyl halide and the disulfide source. Subsurface feeding and use of small diameter tubing is especially desirable; this is believed to provide a longer residence time for the allyl halide. Another advantage provided by subsurface feeding is avoidance of splattering which can occur when, for example, liquid allyl halide strikes the surface of an aqueous mixture.

[0022] Allyl chloride boils in the temperature range in which the processes are conducted. Thus, precautions relating to gaseous reactants and accompanying pressure increases may be necessary when employing allyl chloride as (at least part of) the allyl halide. When at least a part of the allyl halide is allyl chloride and the temperature is at or above the boiling point of allyl chloride, subsurface feeding is especially advantageous. The large pressure increase that would occur with a supersurface feed of allyl chloride is generally avoided by using a subsurface feed of allyl chloride. For example, for a supersurface feed of allyl chloride, when the temperature is at or above its boiling point, an almost instantaneous pressure rise is observed. In a one liter lab reactor, the pressure increase was approximately 15-20 psig (2.05×10^5 to 2.40×10^5 Pa). By comparison, for a subsurface allyl chloride feed under the same conditions, a very gradual internal reactor pressure increase was observed. Without wishing to be bound by theory, it is thought that rising allyl chloride bubbles may have a longer residence time in which to react with the disulfide source, thereby minimizing the amount of allyl chloride that can enter the vapor space of the reactor, and that the bubbles provide for a much greater surface area for

contact and mass transfer between the allyl chloride and the disulfide source in the aqueous phase. Again without wishing to be bound by theory, it is believed that the fast reaction rate usually precludes unreacted allyl chloride from entering the vapor space of the reactor and increasing the vapor space pressure in the reactor.

[0023] It is to be noted that when the term "subsurface" is used anywhere in this document, including the claims, the term does not denote that there must be a vapor space in the reaction zone. For example, if a reaction vessel is completely filled with the stirrable reaction mass, the term "subsurface" means in this case that the substance being fed subsurface is being fed directly into the body of the reaction mass, the surface thereof being defined by the enclosing walls of the reaction vessel.

[0024] Another preferred way of mixing together the allyl halide and the disulfide source-containing aqueous medium is to cofeed them to a reaction zone. By cofeeding the allyl halide and the disulfide source-containing aqueous medium into a reactor or reaction zone, substantial additional advantages are obtained. The advantages of such cofeeding are that the temperature increase which happens during the reaction occurs more slowly, and that the temperature does not rise to as high a value as it does when the allyl halide is fed to the disulfide source-containing aqueous medium. This in turn is less demanding on cooling equipment. Cofeeding should not have an adverse effect on the yield of diallyl disulfide. Each of the various feeds in the cofeed operation may be continuous or intermittent. Further, there is no requirement that any of the feeds occur simultaneously with any of the other feeds. For example, the separate feeds need not start or end at precisely the same time. Instead, there can be a suitably short time between the start of one feed and another, while still realizing the advantages of the cofeed operation. The point here is that the duration of the cofeeds should be sufficient to obtain the foregoing advantages, but need not be exactly coextensive in time.

[0025] One preferred embodiment of the above processes includes the following concurrent operation, namely, continuously, but alternately, withdrawing from at least one and then from at least one other of at least two reaction vessels, a disulfide source-containing aqueous medium at a rate that maintains a continuous stream, and during the withdrawal of such disulfide source-containing aqueous medium from at least one of at least two such reaction vessels, forming additional disulfide source-containing aqueous medium in at least one other of such reaction vessels from which withdrawal is not then

occurring. In this way, disulfide source-containing aqueous medium can be continuously withdrawn from one or more tanks ("Tank(s) I") to serve as a continuous feed, while forming more of such disulfide source-containing aqueous medium in one or more other tanks ("Tank(s) II"), so that when Tank(s) I is/are depleted, the system is switched to Tank(s) II which then serve(s) as the supply for the continuous feed of disulfide source-containing aqueous medium until depleted, and by that time more of such disulfide source-containing aqueous medium has been formed in Tank(s) I. Thus by alternating the supply and the production from one tank (or group of tanks) to another tank (or group of tanks) and switching back and forth between the filled tanks as the supply, a continuous feed of the disulfide source-containing aqueous medium can be maintained without material interruption.

[0026] Another preferred embodiment of the above processes includes the following concurrent operation, namely, continuously withdrawing a disulfide source-containing aqueous medium from a circulating inventory of disulfide source-containing aqueous medium, the withdrawal being at a rate that maintains the continuous feed, and continuously replenishing the circulating inventory from a supply of such disulfide source-containing aqueous medium from a reaction vessel in which disulfide source-containing aqueous medium is produced at least periodically in a quantity sufficient to at least maintain such circulating inventory. By maintaining a circulating inventory of the disulfide source-containing aqueous medium in a pumparound circulation loop, only one reaction vessel is required for forming such disulfide source from an alkali metal sulfide, sulfur, and water.

[0027] Without wishing to be bound by theory, it is believed that the reaction of allyl halide with the disulfide source is almost instantaneous. Thus, long ride times are generally thought to be unnecessary. Stirring on the plant scale is usually in the range of about one hour to about four hours, to ensure good mixing and contact of the allyl halide and the disulfide source.

[0028] Optionally, polyethylene glycol (PEG) may be used in the processes of the invention, although PEG is not required in order to obtain good results. When PEG is used, it is preferably added to the aqueous medium before the allyl halide is mixed with the disulfide source-containing aqueous medium. In fact, PEG can be added before or during the mixing of the alkali metal sulfide and sulfur. Normally and preferably, PEG

with a average molecular weight in the range of about 200 to about 600 is employed.

[0029] Diallyl disulfide is a liquid at both process conditions and ambient conditions. Thus, it normally forms the upper layer of a two-phase mixture, where the lower layer is the aqueous layer. Standard separation methods which are well known in the art, such as decantation, draining of the aqueous layer, drawing off the organic layer, and the like, can be employed to separate the diallyl disulfide (layer) from the aqueous layer. Occasionally, a rag layer is observed between the aqueous layer and the diallyl disulfide layer; the rag layer is usually separated from the diallyl disulfide layer.

[0030] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention. Not all of the parameters, such as the mole ratio of alkali metal disulfide (disulfide source) to allyl halide, were optimized in the following Examples.

EXAMPLE 1

[0031] Two runs were performed. Both runs were conducted in a closed reactor system without the use of an overhead condenser. The 500-gallon (1893 L) reactor had an internal pressure rating of 150 psig (11.4×10^5 Pa) with a PSV set to 100 psig (7.9×10^5 Pa), and vented externally. Variable speed agitation in the reactor was provided by a flat-blade turbine mounted a few feet above a fixed-pitch blade at the bottom of the agitator shaft. Reactor heating and cooling was accomplished by a closed-loop tempered loop on the reactor jacket. The heat transfer fluid was a mixture of Dowtherm G (a mixture of diaryl and triaryl ethers, Dow Chemical Company) and Dowtherm J (a mixture of isomers of an alkylated aromatic compound, Dow Chemical Company). Dowtherm J (from separate chilled or ambient sources) was circulated through a Dowtherm G heated exchanger and then through the reactor jacket. This system was controlled via a DCS (Foxboro) which automatically determined both the source of Dowtherm J (based on set temperature crossover limits) and the degree of heat input (as required) by the Dowtherm G exchanger. Temperature control in the reactor was maintained by entering a temperature set point for the reactor jacket. The allyl chloride was in a portable carbon steel pressure cylinder. A 1 psig (1.1×10^5 Pa) check valve was installed in the feed line at the reactor and a 70 psig (5.4×10^5 Pa) nitrogen pad was maintained on the allyl chloride vessel to prevent backflow into the cylinder. The feed rate of the allyl chloride was manually controlled through a ½-

inch (1.27 cm) small orifice needle valve. Allyl chloride was fed into the reactor via a 0.75-inch (1.9 cm) stainless diptube extending to the parallel plane of the bottom agitator blade. The product diallyl disulfide was filtered through a 10-inch cartridge filter (10 micron, carbon batt/cotton element) after separation from the aqueous and rag layers.

[0032] The reagents used each run were an aqueous sodium hydroxide solution (25 wt%), a sodium sulfide solution (15.8 wt%, VWR International), PEG-600 (polyethylene glycol solution, with an average molecular weight of 600), solid flake 60% sodium sulfide hydrate (Na_2S•2.9 H_2O), solid elemental sulfur powder, and allyl chloride. Amounts of the reagents used for each run are listed in Table 1; yields and product distribution are summarized in Table 2.

[0033] A 25 wt% caustic solution was added to the reactor to provide a 3 wt% initial loading to ensure basic conditions were maintained throughout the process. A 15.8 wt% aqueous solution of sodium sulfide was pumped into the reactor. PEG-600 was pumped into the reactor. A 17 wt% solution of sodium sulfide was achieved by adding solid flake 60% sodium sulfide hydrate to the reactor. Solid elemental sulfur powder was added to the reactor. Air was purged from the reactor by pressuring to 50 psig using nitrogen and venting. Three nitrogen purges were performed. The reactor was heated to 45°C by entering a 45°C set point for the jacket temperature. Visual observations through the sight glass indicated that significant amounts of solid sulfur chunks were floating on the top surface of the reaction mass and appeared stagnant in the dead spaces of the four vertical reactor baffles. During heating, the sulfur completely mixed into the reaction solution with no visible solids present after approximately one hour. The reactor was left overnight with agitation at 45°C.

[0034] Allyl chloride was pressure transferred into the reactor. The subsurface feed mode was utilized to take advantage of the flat-blade gas dispersion turbine since the 45°C reaction temperature was slightly above the boiling point of allyl chloride. The addition of allyl chloride took place at 45°C over a period of approximately three hours. This step was highly exothermic. Temperature conditions inside the reactor remained steady at approximately 43°C with the jacket temperature between 20-22°C; the Dowtherm-J flow rate through the reactor jacket averaged 58,800 lb/hr (26,672 kg/hr). The reactor pressure slowly increased to 10-12 psig ($1.68x10^5$ to $1.84x10^5$ Pa) during the

allyl chloride addition. A two hour agitated post-feed ride at 45°C was employed to achieve complete reaction of the allyl chloride. The reactor was settled without agitation for one hour following the two hour agitated ride period.

[0035] After settling, the dark orange-red clear bottom aqueous phase made up primarily of water, NaCl, unreacted sodium sulfide, and excess NaOH, was removed through a glass phase separation column and discarded. A rag layer (small in volume) of dark, black liquid was observed prior to the organic interface; this rag layer was discarded. The remaining diallyl disulfide product (organic layer) was filtered during transfer to 55-gallon (208 L) product drums. Visual observation of the product through a 1-inch (2.54 cm) sight glass downstream of the filter element indicated that the milky appearance of the product did not diminish. The milky appearance was thought to be from residual water present in the organic phase. Long term settling (2-3 days) did not appear to reduce the turbidity. Addition of molecular sieves to a sample of the milky product appeared to reduce the turbidity after several days of immersion. The turbidity was immediately removed from the sample when passed through a glass column containing a small amount of activated carbon; a clear, slightly yellow product solution was observed. 635 lbs. (288 kg) of neat technical grade diallyl disulfide were recovered. The presence of unreacted allyl chloride was not detected in the diallyl disulfide, and less than 0.1 wt% tetrasulfide was observed in the diallyl disulfide product. Results of this run (Run 1) are summarized in Table 2.

[0036] Run 2 was very similar to Run 1, except for a few items, detailed herein. The amounts of some reagents (see Table 1), the temperature during the allyl chloride feed (42°C), the allyl chloride feed time (2.5 hours) were different. After the nitrogen purge, the reaction mass was heated to 60°C with agitation for two hours, then cooled to 45°C for the allyl chloride feed. After separation of the aqueous layer and the rag layer, and the filtration of the diallyl disulfide, the organic layer (diallyl disulfide) appeared milky yellow in color. The turbidity of the diallyl disulfide gradually turned water clear with a slight yellow tinge. 640 lbs. (290 kg) of neat technical grade diallyl disulfide were recovered. Unreacted allyl chloride was not detected in the diallyl disulfide, and less than 0.1 wt% tetrasulfide was observed in the diallyl disulfide product. Results of this run are summarized in Table 2.

TABLE 1

Run	NaOH, 25%	Na_2S, 15.8%	PEG-600	Na_2S•2.9 H_2O	Sulfur	Allyl chloride	Allyl chloride feed rate*
1	500 lbs. (227 kg)	2831 lbs. (1284 kg)	78 lbs. (35 kg)	100 lbs. (45 kg)	209 lbs. (95 kg)	738 lbs. (335 kg)	4.1 lbs/min (1.9 kg/min)
2	511 lbs. (232 kg)	2828 lbs. (1283 kg)	78 lbs. (35 kg)	100 lbs. (45 kg)	209 lbs. (95 kg)	738 lbs. (335 kg)	4.9 lbs/min (2.2 kg/min)

*Average feed rate.

TABLE 2

Run	Isolated yield[a]	Diallyl monosulfide[b]	Diallyl disulfide[b]	Diallyl trisulfide[b]
1	90.1%	9.0 wt%	87.3 wt%	3.6 wt%
2	90.8%	9.5 wt%	88.0 wt%	3.7 wt%

[a] Based on the amount of allyl chloride fed.
[b] Determined by HPLC.

EXAMPLE 2

[0037] Seven runs were performed. The 2000-gallon (7571 L) reactor was vented. Agitation in the reactor was provided by a variable-pitch three blade paddle agitator and a thermowell/baffle combination. The reactor was configured with a pumparound circulation loop with a 4-inch (10.2 cm) Jogler sight glass located directly below the reactor bottom outlet. Reactor cooling was accomplished by a direct connection of water flow to the jacket from the supply header; a 4-inch (10.2 cm) flow manifold with reduction was constructed to allow two direct supply lines (3-inch and 2-inch; 7.6 cm and 5.1 cm) into the bottom of the reactor for maximum cooling effect. Reactor heating was accomplished with a steam/water mixing valve installed in the utility supply line to the reactor. The solids were fed via a 27-ft^3 (0.76 m^3) stainless-steel conical bottom (60° angle) hopper mounted above the reactor. The hopper was connected to the reactor by an 8-inch (20.3 cm) stainless pipe spool containing an 8-inch (20.3 cm) full port ball valve directly above the reactor, a flexible expansion joint, and an 8-inch (20.3 cm) air-actuated knife valve located directly below the hopper. The solids were charged with the reactor with venting by opening the 8-inch ball valve, then actuating the 8-inch knife valve. The allyl chloride mass feed rate to the reactor was automatically controlled through a ½-inch (1.27 cm) control valve (Badger Meter, Inc.). An "F" trim with linear flow characteristics

was selected to provide the desired nominal flow of 550 lb/hr (7.2 lbmoles/hr; 250 kg/hr) at 50% of trim range. Allyl chloride was fed from a stainless steel horizontal storage vessel. The allyl chloride was fed into the reactor via a ½-inch (1.27 cm) stainless steel diptube extending to approximately 12 inches (30.5 cm) above the parallel plane of the agitator blades. The ½-inch diptube was enclosed in a larger 2-inch (5.1 cm) diameter stainless steel diptube for support to prevent whipping action caused by agitator-induced liquid rotation.

[0038] The reagents used in each run were water, an aqueous sodium hydroxide solution (25 wt%), PEG-600 (polyethylene glycol solution, with an average molecular weight of 600), solid flake 60% sodium sulfide hydrate (Na_2S•2.9 H_2O), solid elemental sulfur powder, and allyl chloride. Amounts of reagents used in each run are listed in Table 3; yields and product distribution are summarized in Table 4.

[0039] The first step of the process was initiated by the addition of approximately 9,584 pounds (4347 kg; 1150 gallons, 4347 L) of water to the reactor. A 25 wt% aqueous NaOH solution was added to ensure that basic conditions were maintained within the reactor. A very small amount of PEG-600 was also added; in this Example, the catalyst (PEG) was reduced to one fourth of the amount used in Example 1 (scaled up and relative to sodium sulfide) for Runs A-F. PEG was not used in Run G, and no detrimental effects on product quality or cycle time were observed. The total sodium sulfide charge was 3,800 pounds (1724 kg), to form the desired 17 wt% aqueous solution. The sodium sulfide was charged from three 1,200-lb (544 kg) supersacks and four 50-lb (23 kg) bags. Each of the three 1,200 lb. supersacks of solid flaked sodium sulfide was individually charged to the reactor through the hopper. After each supersack was charged to the hopper, the hopper dome lid was sealed and nitrogen was applied to pressure the hopper to approximately 8 psig ($1.57x10^5$ Pa). The hopper contents fully discharged in approximately 10-15 seconds with no flow problems. A possible flow problem with the sulfur powder was considered due to the small particle size and bulk density of the sulfur powder. To minimize the possibility of solids bridging in the hopper and resultant flow interruption, the remaining four 50-lb bags of sodium sulfide were charged to the hopper first, and then a single supersack containing 933 lbs (423 kg) of solid elemental sulfur powder was charged to the hopper on top of the sodium sulfide. This charge sequence took advantage of the excellent flow characteristics of the sodium sulfide to initiate flow movement within the hopper. When

the knife valve was actuated, the solids started moving and the sulfur discharged without interruption. Discharge from the hopper to the reactor for this step was also accomplished in 10-15 seconds. No indication of bridging of solids was observed during any of the runs. When the solids additions were finished, the reaction mass was heated to approximately 60°C and allowed to agitate for one hour at that temperature; the reactor contents were circulated through the pumparound loop (bypassing the product filters) once the reaction mass temperature reached 60°C. Visual observation of the 4-inch (10.2 cm) sight glass in the recirculation line indicated that all of the solids were in solution after approximately thirty minutes of agitation. Following the agitated ride period, the reactor was cooled to 45°C with cooling water.

[0040] A dry nitrogen pad at 3-5 psig ($1.22x10^5$ to $1.36x10^5$ Pa) was applied to the allyl chloride and maintained until process operations commenced, at which point the pad pressure was increased to 80 psig ($6.53x10^5$ Pa). Allyl chloride subsurface feed to the reactor was accomplished via pressure transfer, and was immediately started when the reactor temperature reached 45°C. The allyl chloride feed was initiated by setting the automatic flow control valve in manual mode and gradually increasing the valve position to approach the desired flow rate, then the valve was switched to automatic mode. The allyl chloride flow remained constant with a 80 psig ($6.53x10^5$ Pa) head pressure. The allyl chloride addition took place at 45-50°C over a period of approximately six hours. This step was highly exothermic. The internal reactor pressure gradually increased to15-20 psig ($2.05x10^5$ to $2.39x10^5$ Pa)during the six hour allyl chloride feed period. The observed gradual pressure increase was attributed to two things: (1) the vapor space volume was decreasing and being compressed as the liquid volume in the reactor increased, and (2) some nitrogen from the high N_2 pad pressure used to transfer the allyl chloride was released into the reactor (nitrogen is slightly soluble in allyl chloride). A one hour agitated post-feed ride at 45°C was employed to achieve complete reaction of the allyl chloride. The reaction mass was then allowed to settle without agitation for one hour following the one hour agitated ride period at 45°C.

[0041] After settling, the bottom aqueous liquid phase, made up primarily of water, NaCl, unreacted sodium sulfide and excess NaOH, was removed through a 4-inch (10.2 cm) Jogler sight glass and discarded. The aqueous phase appeared as a very dark orange-

red liquid. A rag layer (small in volume) of dark, black liquid was observed prior to the appearance of the organic interface. The reactor was allowed for settle for 10-15 minutes to allow any remaining rag material to settle at the interface. The rag material was drained and discarded. The remaining diallyl disulfide product (organic layer) was sampled during pumparound circulation filtration through a filter housing containing six 30-inch (76.2 cm) 5-micron wound cotton filter elements. The diallyl disulfide was allowed to circulate through the filters for 10-15 minutes then a small sample was collected for analysis. A small liquid sample was collected downstream of the filter housing and analyzed by NMR for sulfide species distribution and the presence of residual allyl chloride. Results are summarized in Table 4. Filtration was continued during the sample analysis period. A 2-inch (5.1 cm) Jogler sight glass was installed in the circulation line downstream of the filter housing to visually observe the product during filtration. The initial appearance of the organic phase in the main 4-inch (10.2 cm) sight glass under the reactor was slightly yellowish and opaque. This remained virtually unchanged after circulation through the filter media; the filter media was required to remove solid particulates from the liquid product. The product was transferred to a bulk storage vessel after confirmation via NMR analysis that the product distribution was within desired specifications. No allyl chloride was detected in the sample.

[0042] The overall cycle time decreased for each successive batch from 22 hours (Run A) to 15 hours (Run G). In Run G, the remaining allyl chloride supply in the stainless steel storage vessel was completely consumed.

TABLE 3

Run	H_2O	NaOH, 25%	PEG-600	$Na_2S \cdot 2.9\ H_2O$	Sulfur	Allyl chloride	Allyl chloride feed rate*
A-F	9584 lbs. (4347 kg)	400 lbs. (181 kg)	125 lbs. (57 kg)	3800 lbs. (1724 kg)	933 lbs. (423 kg)	3595 lbs. (1631 kg)	550 lbs/hr (250 kg/hr)
G	9584 lbs. (4347 kg)	400 lbs. (181 kg)	0 lbs. (0 kg)	3800 lbs. (1724 kg)	933 lbs. (423 kg)	2802 lbs. (1271 kg)	550 lbs/hr (250 kg/hr)

*Average feed rate.

TABLE 4

Run	Isolated yield[a]	Diallyl monosulfide[b]	Diallyl disulfide[b]	Diallyl trisulfide[b]	Diallyl tetrasulfide[b]
A	91.5%	8.5 wt%	86.4 wt%	4.7 wt%	0.21 wt%
B	93.6%	9.0 wt%	85.9 wt%	4.9 wt%	0.20 wt%
C	92.6%	8.6 wt%	86.6 wt%	4.7 wt%	0.17 wt%
D	93.7%	9.1 wt%	86.5 wt%	4.3 wt%	0.12 wt%
E	92.5%	9.0 wt%	86.2 wt%	4.6 wt%	0.20 wt%
F	93.9%	8.1 wt%	86.6 wt%	5.1 wt%	0.25 wt%
G	91.8%	8.6 wt%	87.3 wt%	3.9 wt%	0.11 wt%

[a] Based on the amount of allyl chloride fed.
[b] Determined by NMR.

[0043] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another reactant, a solvent, or *etc.*). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical operation or reaction or in forming a mixture to be used in conducting a desired operation or reaction. Also, even though an embodiment may refer to substances, components and/or ingredients in the present tense ("is comprised of", "comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0044] Also, even though the claims may refer to substances in the present tense (*e.g.*, "comprises", "is", *etc.*), the reference is to the substance as it exists at the time just before it is first contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

[0045] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0046] This invention is susceptible to considerable variation within the spirit and scope of the appended claims.

CLAIMS

1. A process which comprises

A) mixing together sulfur and at least one alkali metal sulfide in an initial aqueous medium in which at least about 90 volume percent of said aqueous medium is water, such that a disulfide source is formed in said initial aqueous medium thereby forming a disulfide source-containing aqueous medium, and

B) mixing together at least a portion of said disulfide source-containing aqueous medium and at least one allyl halide selected from allyl chloride, allyl bromide, allyl iodide, or a mixture of any two or all three of these, in the absence of any additional solvent other than water, at a temperature in the range of about 40°C to about 60°C,

such that diallyl disulfide is formed.

2. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of lithium sulfide, sodium sulfide, potassium sulfide, and a combination of any two or more of the foregoing.

3. A process according to Claim 1 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof.

4. A process according to Claim 1 wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%.

5. A process according to Claim 1 wherein A) is conducted at a temperature in the range of about 40°C to about 65°C.

6. A process according to Claim 1 wherein B) is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

7. A process according to Claim 1 wherein B) is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a reaction zone.

8. A process according to Claim 1 wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

9. A process according to Claim 1 which is conducted in the presence of polyethylene glycol.

10. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of lithium sulfide, sodium sulfide, potassium sulfide, and a combination of any two or more of the foregoing, and wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof.

11. A process according to Claim 10 wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%.

12. A process according to Claim 10 wherein A) is conducted at a temperature in the range of about 40°C to about 65°C.

13. A process according to Claim 10 wherein B) is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

14. A process according to Claim 10 wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

15. A process according to Claim 1 wherein B) is carried out at a temperature in the range of about 45°C to about 50°C.

16. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of lithium sulfide, sodium sulfide, potassium sulfide, and a combination of any two or more of the foregoing, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%, and wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

17. A process according to Claim 16 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

18. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of sodium sulfide, potassium sulfide, and a combination thereof, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein B) is carried out by a process comprising

feeding said allyl halide subsurface to said disulfide source-containing aqueous medium, and wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

19. A process according to Claim 18 wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%.

20. A process according to Claim 18 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

21. A process according to Claim 18 wherein said alkali metal sulfide is sodium sulfide, and wherein said allyl halide is allyl chloride.

22. A process according to Claim 18 wherein B) is carried out at a temperature in the range of about 45°C to about 50°C.

23. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of sodium sulfide, potassium sulfide, and a combination thereof, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and wherein B) is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a reaction zone.

24. A process according to Claim 23 wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%.

25. A process according to Claim 23 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

26. A process according to Claim 23 wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

27. A process according to Claim 23 which is conducted in the presence of polyethylene glycol.

28. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of sodium sulfide, potassium sulfide, and a combination thereof, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein B) is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a

reaction zone, wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%, and wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

29. A process according to Claim 28 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

30. A process according to Claim 28 which is conducted in the presence of polyethylene glycol.

31. A process according to Claim 28 wherein said alkali metal sulfide is sodium sulfide, and wherein said allyl halide is allyl chloride.

32. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of sodium sulfide, potassium sulfide, and a combination thereof, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and wherein said process is conducted in the presence of polyethylene glycol.

33. A process according to Claim 32 wherein the concentration of the alkali metal sulfide in the initial aqueous medium is in the range of about 10 wt% to about 20 wt%.

34. A process according to Claim 32 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

35. A process according to Claim 32 wherein B) is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

36. A process according to Claim 32 wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

37. A process according to Claim 1 wherein said alkali metal sulfide is selected from the group consisting of sodium sulfide, potassium sulfide, and a combination thereof, wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein said process is conducted in the presence of polyethylene glycol, wherein B) is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium, and wherein B) is carried out at a temperature in the range of about 40°C to about 50°C.

38. A process according to Claim 37 wherein A) is carried out at a temperature in the range of about 40°C to about 65°C.

39. A process according to Claim 37 wherein said alkali metal sulfide is sodium sulfide, and wherein said allyl halide is allyl chloride.

40. A process according to Claim 1 wherein at least about 95 volume percent of the aqueous medium is water.

41. A process which comprises mixing together a disulfide source-containing aqueous medium and at least one allyl halide selected from allyl chloride, allyl bromide, allyl iodide, or a mixture of any two or all three of these, in the absence of any additional solvent other than water, at a temperature in the range of about 40°C to about 60°C, such that diallyl disulfide is formed.

42. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof.

43. A process according to Claim 41 wherein said process is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

44. A process according to Claim 41 wherein said process is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a reaction zone.

45. A process according to Claim 41 wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

46. A process according to Claim 41 wherein said process is carried out at a temperature in the range of about 45°C to about 50°C.

47. A process according to Claim 41 which is conducted in the presence of polyethylene glycol.

48. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and wherein said process is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

49. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and

wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

50. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein said process is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium, and wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

51. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and wherein said process is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a reaction zone.

52. A process according to Claim 51 which is conducted in the presence of polyethylene glycol.

53. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein said process is carried out by a process comprising co-feeding said disulfide source-containing aqueous medium and said allyl halide to a reaction zone, and wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

54. A process according to Claim 53 which is conducted in the presence of polyethylene glycol.

55. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, and wherein said process is conducted in the presence of polyethylene glycol.

56. A process according to Claim 55 wherein said process is carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium.

57. A process according to Claim 55 wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

58. A process according to Claim 41 wherein said allyl halide is selected from the group consisting of allyl chloride, allyl bromide, and a combination thereof, wherein said process is conducted in the presence of polyethylene glycol, wherein said process is

carried out by a process comprising feeding said allyl halide subsurface to said disulfide source-containing aqueous medium, and wherein said process is carried out at a temperature in the range of about 40°C to about 50°C.

59. A process according to Claim 41 wherein at least about 95 volume percent of the aqueous medium is water.

INTERNATIONAL SEARCH REPORT

In pplication No
PCT/US2004/022596

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C319/16 C07C321/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198703 Derwent Publications Ltd., London, GB; Class E19, AN 1987-019889 XP002304099 & RO 89 670 A (PLAFAR INTR) 30 June 1986 (1986-06-30) abstract -----	1-59
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HASE, T. A. ET AL: "A convenient synthesis of symmetrical disulfides" XP009039428 retrieved from STN Database accession no. 1983:178688 abstract -/--	1-59

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
1 June 2005	15/06/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Lorenzo Varela, M.J.

INTERNATIONAL SEARCH REPORT

Application No
PCT/US2004/022596

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& SYNTHETIC COMMUNICATIONS , 12(12), 947-50 CODEN: SYNCAV; ISSN: 0039-7911, 1982,	
Y	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WANG, JIN-XIAN ET AL: "A facile method for the syntheses of dialkyl disulfides from sulfur under phase transfer conditions" XP009039429 retrieved from STN Database accession no. 1995:827623 abstract & SYNTHETIC COMMUNICATIONS , 25(22), 3573-81 CODEN: SYNCAV; ISSN: 0039-7911, 1995,	1-59
Y	GLADYSZ, J. A. ET AL: "New methodology for the introduction of sulfur into organic molecules. Synthesis of anhydrous dilithium sulfide, dilithium disulfide and lithium thiolates by lithium triethylborohydride reduction of elemental sulfur and disulfides" TETRAHEDRON , 35(20), 2329-35 CODEN: TETRAB; ISSN: 0040-4020, 1979, XP002304096 *the examples*	1-59
Y	PATENT ABSTRACTS OF JAPAN vol. 0144, no. 92 (C-0773), 26 October 1990 (1990-10-26) & JP 02 204487 A (NKK CORP), 14 August 1990 (1990-08-14) abstract	1-59
Y	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; XP002304131 retrieved from CA accession no. 1975:170041 Database accession no. DN 82:170041 abstract	1-59

INTERNATIONAL SEARCH REPORT

International Application No	PCT/US2004/022596

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
RO 89670 A	30-06-1986	RO 89670 A2	30-06-1986
JP 02204487 A	14-08-1990	NONE	