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(54) Title: METHOD FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION IN CONDENSER AND COMPRESSION SYSTEMS

(57) Abstract

A method is provided for inhibiting the polymerization of vinyl aromatic monomers in ethyl benzene dehydrogenation effluent condenser systems and in styrene-water separator vent gas compressor systems. The method comprises adding a combination of a phenol compound and a hydroxylamine compound to the effluent stream of an ethyl benzene dehydrogenation reactor and to the styrene-water separator vent gas stream to inhibit polymerization of monomers in reactor effluent condenser systems and vent gas compressor systems.

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METHOD FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION IN CONDENSER AND COMPRESSION SYSTEMS

FIELD OF THE INVENTION

The present invention relates to methods of inhibiting undesired polymerization of vinyl aromatic monomers during cooling and condensation of ethylbenzene dehydrogenation effluent and during compression of vent gases from the styrene-water separator in a process to produce styrene from ethylbenzene.

BACKGROUND OF THE INVENTION

Polystyrene is a thermoplastic with many desirable characteristics. It is clear, transparent, readily colored and easily fabricated. The family of styrene polymers includes polystyrene itself, copolymers of styrene with other vinyl monomers, polymers of derivatives of styrene and mixtures of polystyrene and styrene-containing copolymers with elastomers.

ABS (acrylonitrile, butadiene-styrene) resins have enjoyed tremendous commercial popularity for many years as durable, temperature and solvent resistant elastomers. Styrene plastics are commonly used for packaging, including foams and films, coatings, in appliance fabrication, for housewares and toys, lighting fixtures and in construction materials.

It is well known that styrene monomer readily polymerizes when heated or exposed to light. Heat polymerization is rapid and increases with increasing temperature. This polymerization is undesirable during many stages of the manufacturing, processing, handling, storage and use of styrene monomers.

A particular problem exists during the reaction process which produces styrene from ethylbenzene. The major commercial process for the production of styrene consists of two reactions. In the first reaction, ethylbenzene is formed by alkylation of benzene with ethylene. In the second reaction ethylbenzene is dehydrogenated to produce styrene. During the dehydrogenation step ethylbenzene is vaporized and mixed with steam prior to entering a reactor. The temperatures inside the reactor reach in excess of 1,000°F. The reactor converts ethylbenzene to styrene and hydrogen. The heat from the reactor effluent is recovered in a first heat exchanger which produces low pressure steam. The reactor effluent does not condense in the first heat exchanger but the effluent temperature is reduced to between 200°F to 400°F. The effluent is condensed in one or more subsequent condensers that are cooled with a cooling medium. The condensed effluent is sent to a settling drum where a water stream and a crude styrene stream are separately bled from the settling drum. The crude styrene stream is sent to a distillation system to distill styrene and water from the crude styrene stream. It is well known to add polymerization inhibitors to the crude styrene stream prior to distillation to inhibit polymerization in the distillation unit. However, the distillation process is not the only process which suffers monomer polymerization problems.

The ethylbenzene dehydrogenation reactor effluent stream contains from about 20% to 30% styrene and thus is capable of forming

polymer deposits during condensation. Polymer adheres to condenser surfaces limiting throughput and heat transfer, thus necessitating periodic cleaning and maintenance of condenser surfaces.

Another area which suffers from monomer polymerization problems is the styrene-water separator vent gas compressor system. The non-condensables from the styrene-water settling drum are compressed in a vent gas compressor system and sent to a boiler as fuel. The gas stream entering the compressor system generally contains from about 20% to 30% styrene. Unsaturated monomers in the vent gas can polymerize during compression resulting in a polymer coating on compressor equipment.

Therefore, a need exists for an effective polymerization inhibitor which is effective to inhibit polymerization of monomers in ethylbenzene effluent condenser systems and vent gas from the styrene-water separator.

PRIOR ART

U.S. Patent 3,864,307 to Nast et al. discloses stabilizers of natural and synthetic diene polymers with cresol derivatives.

U.S. Patent 4,409,408 to Miller discloses stabilization of vinyl aromatic compounds against polymerization by use of N,N-dialkylhydroxylamine and tertiary alkylcatechols.

U.S. Patent 4,744,881 to Reid discloses antioxidant materials to inhibit fouling in petroleum and petrochemical operations. The antioxidant materials are composed of non-hindered or partially hindered phenols in combination with a strongly basic material such as an organoamine.

U.S. Patent 4,929,778 to Roling discloses methods and compositions for inhibiting styrene monomer polymerization during elevated temperature processing and during storage. The compositions comprise a combination of phenylenediamine compound and a hindered phenol compound.

U.S. Patent 5,128,022 to Reid discloses methods and compositions for inhibiting polymer formation in petroleum or petrochemical processes. The compositions comprise a combination of N-phenyl-N'-(1,3-dimethylbutyl-)-p-phenylenediamine and an organic acid.

U.S. Patent 5,221,461 to Henrici et al. discloses a method for inhibiting fouling during elevated temperature processing of hydrocarbons. The method comprises adding a catechol having a specified structure and an organic acid to the hydrocarbon as an antioxidant composition to inhibit fouling.

U.S. Patent 5,221,498 to Reid et al. discloses methods and compositions for inhibiting polymerization of a vinyl monomer during processing, shipment or storage. The compositions comprise a combination of dihydroxybenzene compound and an organic amine compound.

U.S. Patent 5,282,957 to Wright et al. discloses the use of hydroxyalkylhydroxylamine compounds to prevent polymerization of hydrocarbons during processing and storage.

U.S. Patent 5,396,004 to Arhancet et al. discloses the use of a combination of phenylenediamine compound and a hydroxyl amine which is preferably a hydroxyalkyl-hydroxylamine compound to inhibit polymerization of vinyl aromatic monomers under distillation conditions.

U.S. Patent 5,396,005 to Arhancet discloses the use of a methoxyphenol compound consisting of eugenol and 2-tert-butyl-4-hydroxyanisol and a phenylenediamine compound to inhibit polymerization of ethylenically unsaturated monomers.

U.S. Patent 5,426,257 to Arhancet discloses oxime compounds and a hydroxylamine compound and, alternatively, an oxime compound, a hydroxylamine compound and a phenylenediamine compound as polymerization inhibitors for vinyl aromatic monomers in oxygen-free processing systems.

U.S. Patent 5,446,220 to Arhancet discloses the use of a combination of a dinitrophenol compound, a hydroxylamine compound and a phenylenediamine compound as polymerization inhibitors for vinyl aromatic monomers in oxygen-free processing systems.

U.S. Patent 5,470,440 to Arhancet discloses the use of 2,6-di-tert-butyl-4-methylphenol and substituted benzoquinonediimide compounds as vinyl aromatic monomer polymerization inhibitors.

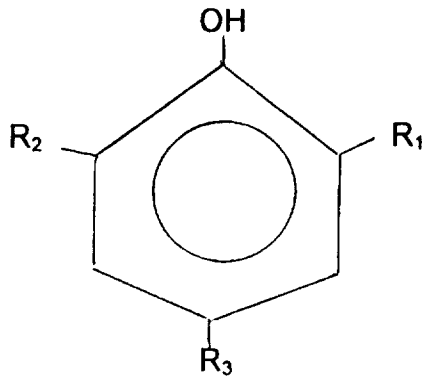
U.S. Patent 5,510,547 to Arhancet et al. discloses methods for inhibiting the polymerization of vinyl aromatic monomers in oxygen-free processing systems. The methods comprise adding a combination of a hydroxylamine compound and a phenylenediamine compound to the vinyl aromatic monomer.

SUMMARY OF THE INVENTION

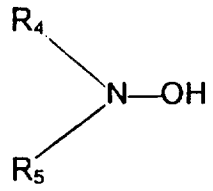
The present invention provides a method for inhibiting the polymerization of vinyl aromatic compounds in ethylbenzene dehydrogenation effluent condenser systems and styrene-water separator vent gas compressor systems during production of styrene from ethylbenzene. The method comprises adding a hindered phenol compound and a hydroxylamine compound to the effluent from ethylbenzene dehydrogenation reactors and to styrene-water separator vent gases in amounts sufficient to inhibit polymerization of vinyl aromatic monomers during reactor effluent condensation and vent gas compression.

DESCRIPTION OF THE INVENTION

The present invention provides a method for inhibiting the polymerization of vinyl aromatic compounds in ethylbenzene dehydrogenation effluent condenser systems and styrene-water separator vent gas compressor systems during the production of styrene from ethylbenzene. The method comprises adding a combination of a) a phenol or mixture of phenols having the formula:



wherein R_1 and R_2 may be the same or different, with R_1 and R_2 being independently selected from the group of C_1-C_{20} alkyl, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl and H with the proviso that R_1 and R_2 may not both be H; R_3 is selected from the group of C_1-C_{20} alkyl, C_1-C_{40} alkanoic acid ester, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl, C_1-C_6 alkylamino, C_1-C_6 alkoxy, amine, polynuclear aryl and substituted polynuclear aryl; and b) a hydroxylamine having the formula:



wherein R_4 and R_5 are the same or different and are hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl or aralkyl groups with the proviso that R_4 and R_5 may not both be H, both be methyl - or be a methyl - when the other is H, to ethylbenzene dehydrogenation reactor effluent and to styrene-water separator vent gases to inhibit polymerization of unsaturated monomers in ethylbenzene dehydrogenation reactor effluent condenser systems and styrene-water vent gas compressor systems during production of styrene from ethylbenzene.

In accordance with this invention the phenols are hindered and partially hindered phenols or mixtures thereof such as:

2,6-di-t-butyl-4-methylphenol
and octadecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate.

These three hindered phenols are all commercially available.

Other representative hindered phenol compounds include:

4,4'-methylenebis(2,6-di-t-butylphenol)
1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene
2,6-di-t-butyl-α-dimethylamino-p-cresol
2,6-di-t-butyl-4-secbutylphenol
2,2'-methylenebis(4-ethyl-6-t-butylphenol)
2,2'-methylenebis(4-methyl-6-t-butylphenol)
2,2'-methylenebis(6-(1-methylcyclohexyl)-p-cresol; and
2,2'-methylenebis(4-methyl-6-cyclohexylphenol)

In accordance with structural formula I supra the preferred hindered phenols are those wherein R_1 and R_2 are chosen from the C_1-C_{20} tert-alkyl and C_1-C_{20} alkyl with R_3 being chosen from C_1-C_{20} alkyl, or C_1-C_{40} alkanoic acid ester.

The most preferred hindered phenol is 4-methyl-2,6-di-tert-butyl phenol (BHT).

The partially hindered phenols include, but are not limited to, p-cresol, p-methoxyphenol, -p-amino-phenol, and p-(p-methoxybenzylidene-amino) phenol. The most preferred partially hindered phenol is 2-tert-butyl-4-methoxyphenol (butylated hydroxyanisole or BHA).

Examples of suitable hydroxylamines include:

N-ethylhydroxylamine
N,N-diethylhydroxylamine
N-(2-hydroxybutyl)hydroxylamine
N-(2-hydroxyethyl)hydroxylamine
N-(2-hydroxypropyl)hydroxylamine
N,N-di-n-propylhydroxylamine
N,N-di-n-butylhydroxylamine
N,N-diphenylhydroxylamine
N-benzylhydroxylamine
N,N-bis(ethylbenzyl)hydroxylamine
N,N-bis(m-ethylbenzyl)hydroxylamine
N,N-bis-(p-ethylbenzyl)hydroxylamine

or mixtures thereof. Preferably, the hydroxylamine is N,N-bis(hydroxypropyl)hydroxylamine, also called hydroxypropylhydroxylamine (HPHA). The most preferred hydroxylamine is diethylhydroxylamine (DEHA).

The phenol compounds and the hydroxylamine compounds cannot be added to the ethylbenzene stream fed to the dehydrogenation reactor due to the danger that the high temperatures in the reactor will decompose the phenol and hydroxylamine compounds and thereby degrade their efficacy as polymerization inhibitors.

The phenol and hydroxylamine compounds are preferably added separately to the effluent stream from the ethylbenzene dehydrogenation reactor and to the styrene-water vent gas compressor system in sufficient amounts to inhibit polymerization.

Representative dehydrogenation effluent stream and styrene-water vent gas stream compositions are shown in Tables A and B.

TABLE A

Representative Ethylbenzene Dehydrogenation Effluent Stream Composition

Component	Percent by Weight
hydrogen	1
carbon dioxide	1
benzene	1
toluene	2
styrene	20-30
ethylbenzene	10-20
water	50-70

TABLE B

Representative Styrene-Water Vent Gas Compressor Feed Stream Composition

Component	Percent by Weight
hydrogen	10-15
carbon dioxide	5-10
methane	5
ethane	5
benzene	5
toluene	5
styrene	20-30
ethylbenzene	20-30
xylene	1
water	20-30

For a polymerization inhibitor to be effective in inhibiting vinyl monomer polymerization in streams containing greater than about 20% by weight water such as shown in Tables A and B, the inhibitor must contain oil and water soluble actives as does the present invention.

The amount of phenol and hydroxylamine components effective to inhibit polymerization will depend upon the conditions of each feed stream, each reactor effluent condenser system and each vent gas compressor system. However, it is expected that from about 1 to 1000 parts per million (ppm), and preferably from about 1 to 100 ppm, of the combined phenol and hydroxylamine compounds in the reactor effluent and in the vent gas will effectively inhibit polymerization of vinyl aromatic monomers. The ratio of phenol to hydroxylamine effective to inhibit monomer polymerization is about 2:1 to 1:2.

The invention will now be further described with reference to a specific example which is to be regarded solely as illustrative and not as restricting the scope of the invention.

Example

Uninhibited styrene (25 mL), water (25 mL), and toluene (50 mL) were placed in a round bottomed flask fitted with a condenser. An amount of polymerization inhibitor was added to the flask and the mixture was refluxed for two hours. The water was separated in a separatory funnel and 15 mL of toluene/styrene organic phase was measured. Methanol (40 mL) was added to the sample to precipitate any polystyrene present and the amount of polystyrene was measured. The results are shown in Table C.

TABLE C

Treatment	Dose (ppm)	Percent by Weight of Polymer
Blank	------	1.28
BHT/BHA	37.5/12.5	0.06
BHT/BHA	18.7/6.3	0.58
BHT/DEHA	12.5/12.5	0.20
BHT/BHA/DEHA	9/3/13	0.18

where:

BHT is 4-methyl-2,6-di-tert-butyl phenol

BHA is 2-tert-butyl-4-hydroxyanisole

DEHA is diethylhydroxylamine

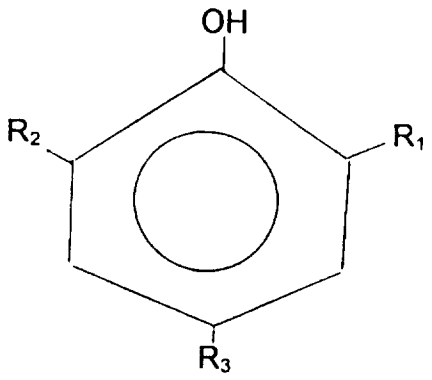
Table C shows that when the invention inhibitors of a hindered phenol and a hydroxylamine (BHT/DEHA) or a phenol mixture and a hydroxylamine (BHT/BHE/DEHA) were added to a system containing 20% by volume water that the invention inhibitors inhibited polymerization better than a mixture of phenols alone (BHT/BHA) and better than the blank.

Table C also shows that adding a hindered phenol compound and a hydroxylamine compound to a water, styrene and hydrocarbon mixture similar to what is expected in ethylbenzene dehydrogenation reactor effluent streams and styrene-water separator vent gas streams that the invention inhibitors effectively inhibited polymerization of styrene at elevated temperatures.

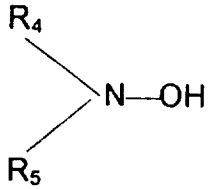
While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

We Claim:

1. A method for inhibiting the polymerization of vinyl aromatic compounds during compression or condensation of a stream comprising vinyl aromatic compounds and water, said method comprising adding to said stream an effective polymerization inhibiting amount of a combination of a) a phenol or mixture of phenols having the formula:



wherein R_1 and R_2 may be the same or different, with R_1 and R_2 being independently chosen and selected from the group of C_1-C_{20} alkyl, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl and H with the proviso that R_1 and R_2 may not both be H; R_3 is selected from the group of C_1-C_{20} alkyl, C_1-C_{40} alkanoic acid ester, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl, C_1-C_6 alkylamino, C_1-C_6 alkoxy, amine, polynuclear aryl and substituted polynuclear aryl; and b) a hydroxylamine having the formula:



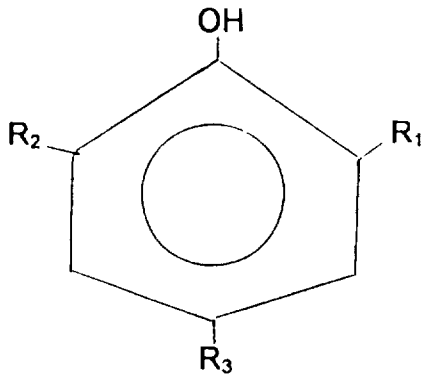
wherein R_4 and R_5 are the same or different and are selected from the group consisting of hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl and aralkyl groups with the proviso that R_4 and R_5 may not both be H, both be methyl - or one be a methyl - when the other is H.

2. The method of claim 1 wherein said vinyl aromatic compounds are styrene monomers.

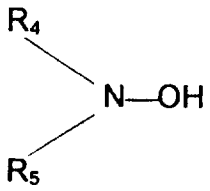
3. The method of claim 1 wherein (a) and (b) are present in a weight ratio of from about 2:1 to 1:2.

4. The method of claim 1 wherein said effective polymerization inhibiting amount of said composition is from about 1 to 1000 parts of said composition per million parts of said ethylbenzene dehydrogenation reactor effluent condenser stream or said styrene-water vent gas compressor stream.

5. A method for inhibiting the polymerization of vinyl aromatic compounds during compression or condensation of a stream, said method comprising adding to a stream an effective polymerization inhibiting amount of a composition comprising a) a phenol or mixture of phenols having the formula:



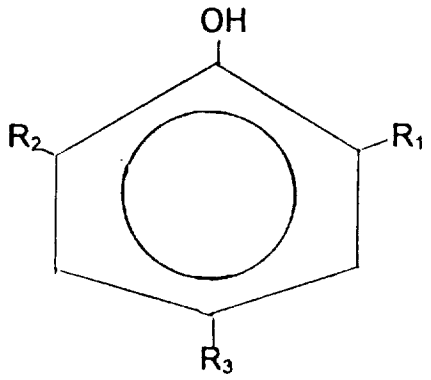
wherein R_1 and R_2 may be the same or different, with R_1 and R_2 being independently chosen and selected from the group of C_1-C_{20} alkyl, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl and H with the proviso that R_1 and R_2 may not be the same when R_1 or R_2 is H; R_3 is selected from the group of C_1-C_{20} alkyl, C_1-C_{40} alkanoic acid ester, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl, C_1-C_6 alkylamino, C_1-C_6 alkoxy, amine, polynuclear aryl and substituted polynuclear aryl; and b) a hydroxylamine having the formula:



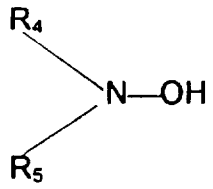
wherein R_4 and R_5 are the same or different and are hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl or aralkyl groups with the proviso that R_4 and R_5 may not both be H, both be methyl - or one be a methyl - when the other is H, wherein said stream is comprised of hydrogen, carbon dioxide, benzene, toluene, styrene, ethylbenzene, water, optionally methane, optionally ethane, and optionally xylene.

6. A method for inhibiting the polymerization of vinyl aromatic compounds in an ethylbenzene dehydrogenation effluent condenser system comprising adding to an ethylbenzene dehydrogenation reactor

effluent condenser stream an effective polymerization inhibiting amount of a combination of a) a phenol or mixture of phenols having the formula:

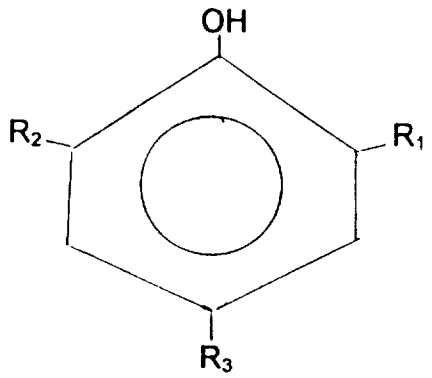


wherein R_1 and R_2 may be the same or different, with R_1 and R_2 being independently chosen and selected from the group of C_1-C_{20} alkyl, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl and H with the proviso that R_1 and R_2 may not both be H; R_3 is selected from the group of C_1-C_{20} alkyl, C_1-C_{40} alkanoic acid ester, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl, C_1-C_6 alkylamino, C_1-C_6 alkoxy, amine, polynuclear aryl and substituted polynuclear aryl; and b) a hydroxylamine having the formula:

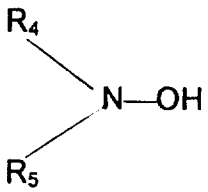


wherein R_4 and R_5 are the same or different and are selected from the group consisting of hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl and aralkyl groups with the proviso that R_4 and R_5 may not both be H, both be methyl - or one be a methyl - when the other is H.

7. A method for inhibiting the polymerization of vinyl aromatic compounds in a styrene-water separator vent gas compressor system comprising adding to a styrene-water vent gas compressor stream an effective polymerization inhibiting amount of a combination of a) a phenol or mixture of phenols having the formula:



wherein R_1 and R_2 may be the same or different, with R_1 and R_2 being independently chosen and selected from the group of C_1-C_{20} alkyl, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl and H with the proviso that R_1 and R_2 may not both be H; R_3 is selected from the group of C_1-C_{20} alkyl, C_1-C_{40} alkanoic acid ester, C_1-C_{30} alkaryl, substituted C_1-C_{30} alkaryl, C_1-C_6 alkylamino, C_1-C_6 alkoxy, amine, polynuclear aryl and substituted polynuclear aryl; and b) a hydroxylamine having the formula:



wherein R_4 and R_5 are the same or different and are selected from the group consisting of hydrogen, hydroxyalkyl, alkoxyalkyl, alkyl, aryl, alkaryl and aralkyl groups with the proviso that R_4 and R_5 may not both be H, both be methyl - or one be a methyl - when the other is H.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/11303

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07C 7/20; C10G 9/16
US CL : 585/5, 24; 208/48AA
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)

U.S. : 585/5, 24; 208/48AA

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

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,470,440 A (ARHANCET) 28 November 1995, column 2, first full paragraph.	1-7
X	US 4,744,881 A (REID) 17 May 1988, column 4, lines 35-40 AND 52-66.	1-7
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Y		1-7
Y	US 4,929,778 A (ROLING) 29 May 1990, column 2, lines 1-65	1-7
Y	US 4,409,408 A (MILLER) 11 October 1983, see the abstract.	1-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 AUGUST 1997	30 OCT 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ELIZABETH WOOD Telephone No. (703) 308-0661

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