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"PROCESS FOR INHIBITING POLYMERIZATION DURING
DISTILLATION OF VINYL AROMATICS" ✓

FIELD

5 This invention relates to a process for inhibiting the polymerization of vinyl aromatic compounds such as styrene during the distillation of said compounds, by adding to the vinyl aromatic compound a nitroso compound such as N-nitroso-N, N'-di-3-pentyl-p-phenylenediamine.

BACKGROUND

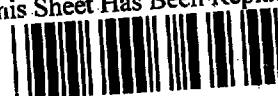
10 Styrene is one of several vinyl aromatic compounds which has considerable commercial utility. Styrene is polymerized into polystyrene which is a clear, readily colored and easily fabricated plastic with many uses. The efficiency of the polymerization process is dependent on the purity of the monomer starting material. Since the processes for producing styrene, and other vinyl aromatic compounds, will contain various reaction products including
15 benzene, toluene, etc., the mixture is distilled to separate these undesirable contaminants. Unfortunately, the temperatures required for distillation, typically 90 to 150°C, leads to the polymerization of the vinyl aromatic compounds. In order to minimize or prevent polymerization of the vinyl aromatic monomer, it is common to add a polymerization inhibitor to the distillation mixture.

20 The art discloses a variety of compounds which are claimed to inhibit polymerization. US-A-4,050,993 discloses the use of N,N-nitroso-methylaniline as

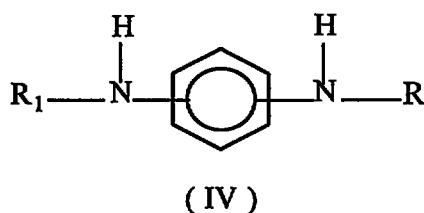


a polymerization inhibitor. US-A-3,988,212 discloses the use of N-nitrosodiphenyl amine in combination with dinitro-o-cresol. US-A-4,013,580 discloses the use of N-nitroso aniline derivatives. US-A-4,341,600 discloses the use of a mixture of dinitro-p-cresol and N-nitroso-diphenyl amine. US-A-4,654,451 discloses alkyl substituted p-nitroso phenol in combination with p-nitroso phenol. US-A-5,034,156 discloses N-nitrosophenyl-hydroxylamine plus hydroquinone monomethyl ether. US-A-5,396,004 discloses a phenylene-diamine compound plus a hydroxyalkylhydroxyl-amine compound. US-A- 5,254,760 discloses 1-oxy-2,2,6,6-tetramethylpiperidine plus an aromatic nitro compound. US-A-4,929,778 discloses a phenylenediamine compound plus a hindered phenol compound. US-A-5,312,952 discloses the use of the reaction product of a C₉-C₂₀ alkyl phenol with sulfuric and nitric acid and optionally an aryl or alkyl-substituted phenylenediamine. WO9503263 discloses 3,5-di-tert-butyl-4-hydroxy-N,N-dimethyl benzyl amine. EP-A-697386 discloses 4-acetylamino-2,2,6,6-tetramethyl piperidine N-oxyl in combination with 4-nitroso phenol. JP-A-0701910 discloses phosphite compounds, nitrosoamine compounds or phenol compounds. JP-A-05310815 which discloses the ammonium salt of N-nitrosophenyl hydroxylamine. JP-A-03149205 discloses nitrosophenols plus dicyclohexyl-ammonium nitrate. JP-A-1226858 which discloses the use of substituted nitrosobenzene. US-A-4,967,027 discloses p-nitroso phenol plus p-t-butyl catechol. JP-A-59029624 which discloses the use of N-nitroso compound, e.g., N-nitroso-diphenylamine and a catechol, e.g., p-t-butylcatechol.

In contrast to these compounds, a series of compounds have now been found which are particularly effective in inhibiting the polymerization of vinyl aromatic compounds in general and styrene in particular. These compounds are



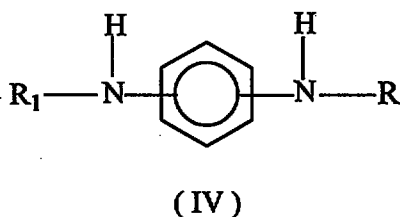
the N-nitroso derivatives of unsubstituted or dialkyl substituted phenylenediamine having the following structure:



- 5 Both the mono and di-nitroso derivatives are useful as inhibitors. The compounds can be used by themselves or in combination with phenylenediamine.

SUMMARY

- 10 This invention relates to a process for inhibiting the polymerization of a vinyl aromatic compound during its distillation. One embodiment of the process involves adding to the vinyl aromatic compound an effective amount of the reaction product of nitrous acid and an amine having the formula:



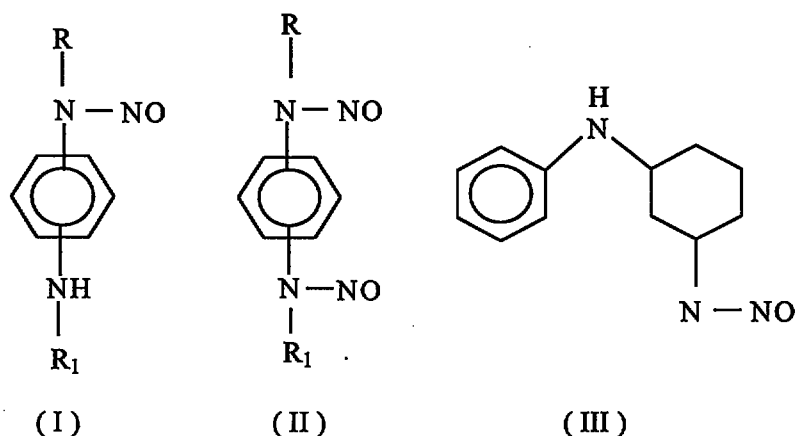
where R and R₁ are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

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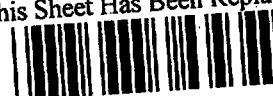
Another embodiment is a process for inhibiting the polymerization of a vinyl aromatic compound during the distillation of the vinyl aromatic compound comprising adding to the compound an effective amount of a nitroso compound selected from the group consisting of:

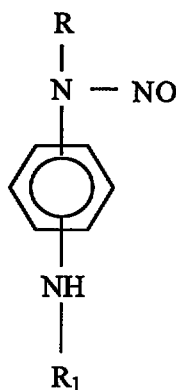
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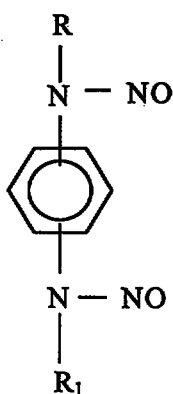
and mixtures thereof where R and R_1 are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

10 Yet another embodiment is a process for inhibiting the polymerization of a vinyl aromatic compound during the distillation of the vinyl aromatic compound comprising adding to the compound an effective amount of a mixture of inhibitor compounds having structures I, II and IV:

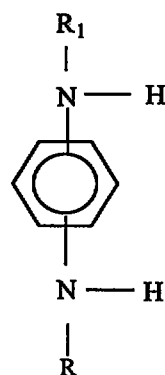




(I)



(II)



(IV)

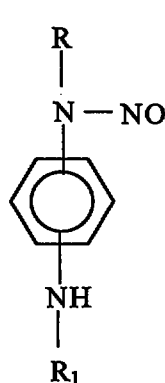
where R and R₁ are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

DETAILED DESCRIPTION

The present invention relates to a process for inhibiting the polymerization of a vinyl aromatic compound during its distillation. Vinyl aromatic compounds to which the instant process is applicable include styrene, alpha-methyl styrene, divinylbenzene, vinyl toluene, vinyl naphthalene and polyvinyl-benzene.

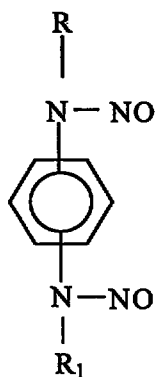
The process generally involves adding an inhibitor compound to the vinyl aromatic compound during its distillation. The inhibitor compounds which can be used in the present process include nitroso compounds selected from the group consisting of structures I, II, III and mixtures thereof.





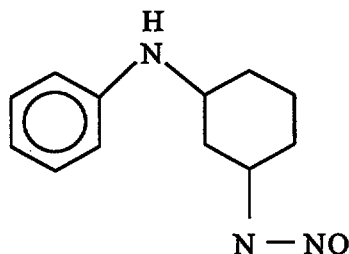
(I)

N-nitroso-dialkyl
phenylenediamine



(II)

N,N'-dinitroso-
dialkylphenylene-
diamine

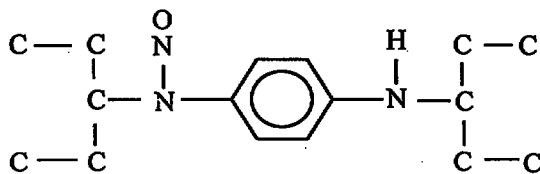


(III)

N-phenyl, N'-nitroso-1,4-
diamino cyclohexane

The R and R₁ groups can each be hydrogen or an alkyl group having from 1 to 18 carbon atoms. Illustrative of the alkyl groups which can be used are methyl, ethyl, propyl, butyl, pentyl, octyl, decyl, sec-butyl, iso-propyl and isopentyl.

- 5 Included in structures I and II above are the o, m and p isomers. Preferred compounds encompassed within structures I and II are the following compounds having structure IA and IIA.

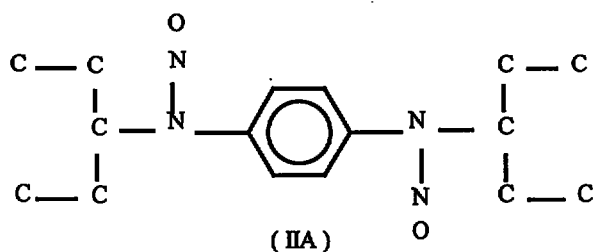


(I A)

N-nitroso-N,N'-di-3-pentyl-p-phenylenediamine

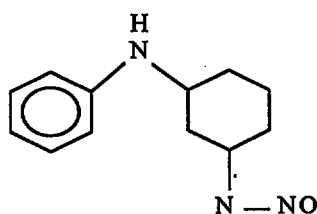
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N,N'-dinitroso-N,N'-di-3-pentyl-p-phenylenediamine

Another nitroso compound which can be used as a polymerization inhibitor is N-phenyl, N'-nitroso-1,4-diamino cyclohexane which has structure III below.



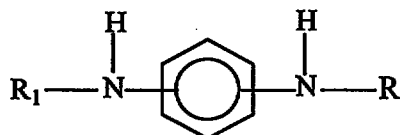
(III)

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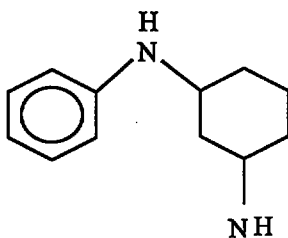
The nitroso compounds are prepared by reacting nitrous acid with an amine. The amine used to obtain these compounds have structures (IV) and (V) below.

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(IV)



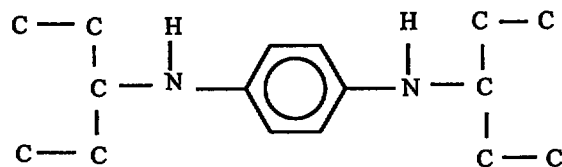
(V)

The reaction of nitrous acid with an amine is well known in the art and is included here for completeness. Generally, the amine is reacted with nitrous acid at a temperature of -10°C to 10°C . The nitrous acid can be added or it can be generated in situ by adding sodium nitrite and hydrochloric acid. Further, in the case of a diamine, the amount of nitrous acid added will determine whether the mono or dinitroso compounds are obtained. However, even if a 1:1 stoichiometric amount of nitrous acid:amine is added, a mixture of the mono and dinitroso compounds may still be obtained. Accordingly, the exact nature of the reaction product may not be known. The reaction product may contain both mono and dinitroso compounds along with unreacted amine. In fact, the unreacted amine can act as a solvent for the nitroso compound.

In a preferred embodiment, the amine is N,N'-di-3-pentyl-p-phenylene-diamine which is represented by structure (IVA) below.

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(IV A)

The reaction product may contain compounds IA, IIA and IVA.

5 It is, therefore, one embodiment of the present invention to use the reaction product described above as the polymerization inhibitor. Alternatively, the pure components can be isolated and used either individually or in combination with each other. The separate components can be isolated by means well known in the art such as fractional crystallization, liquid chromatography and column
10 chromatography.

In order to adequately prevent polymerization of the vinyl aromatic compounds, an effective amount of the nitroso compound or mixtures thereof must be used. For the nitroso compound having structures I and III, an effective amount varies from 1 to 1000 wt. ppm. If the nitroso compound has structure (II),
15 then the effective amount varies from 1 to 1000 ppm. When mixtures of compounds (I) (II) and (IV) are used the amounts of each component in the mixture varies as follows: compound I varies from 18 to 96 wt.%, compound II varies from 2 to 50 wt.% and compound IV varies from 2 to 80 wt.%. The amount of the mixture which is added to the vinyl aromatic compound varies from 1 to
20 1000 wt. ppm.

The reaction product of the amine and nitrous acid can be used as is without further purification. Thus when the amine is represented by structure IV, the reaction product may contain compounds I, II, IV plus other compounds and



the amount of the reaction product which is added to the vinyl aromatic compound varies from 1 to 1000 wt. ppm.

Having added the effective amount of inhibitor to the mixture containing the vinyl aromatic compound, the mixture is distilled at a temperature of 65 to 150°C in standard distillation columns. The distillation temperature can be controlled by controlling the pressure in the column from 1 to 53kPa. Further, the inhibitor may be added to the vinyl aromatic compound in any convenient manner. Usually the inhibitor is added in liquid form by periodically or continuously adding the required amount to the inlet distillation feed. In this respect, if the inhibitor is a solid, it is dissolved in an appropriate solvent. Illustrative of the solvents which can be used are toluene, benzene, ethylbenzene, xylenes, etc. Preferred solvents are ethylbenzene or the starting amine which allows for easy separation from the purified vinyl aromatic compound.

EXAMPLE 1

In a round bottom flask, there were placed 2.1 g of N, N'-di-3-pentyl-p-phenylenediamine obtained from UOP and identified as UOP No. 5[®]. To this flask, which was chilled to 0°C, there were added 50 mL of a hydrochloric acid solution composed of equal parts water and concentrated hydrochloric acid. Next a solution of 0.51g sodium nitrite in 12 mL of water were added over a twenty minute period. Any excess acid was now neutralized with a chilled solution of sodium hydroxide. The resultant mixture was poured into a separatory funnel to which there were added 100 mL of ethyl ether. The organic phase was collected, dried and the ethyl ether removed by use of a rotary evaporator. The isolated product was a dark colored liquid which was identified as sample A.



EXAMPLE 2

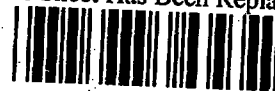
The following test procedure was used to determine the ability of sample A to inhibit the polymerization of styrene. Five glass ampules were filled with 5 g of styrene and 250 wt. ppm of sample A. Four ampules were placed in an oil bath heated to 120°C. The fifth ampule was analyzed to give the initial amount of polymerization. One ampule was removed at 1 hour increments and the contents filtered to determine the amount of polystyrene which was formed. These results are presented below. The experiment was repeated except that the amount of sample A was changed each time to provide results for 175, 125 and 75 wt. ppm. Dinitro-butyl-phenol (DNBP) and dinitro-phenol (DNP) were also tested in the same manner to provide comparative examples below and those results are also presented.

Polymerization Inhibitor Activity of Various Inhibitors

Sample ID	% Polymerization				
	Initial	1 hour	2 hours	3 hours	4 hours
Sample A (250 ppm)	0	0	0	0	0
Sample A (175 ppm)	0	0	0.3	0.1	1.3
Sample A (125 ppm)	0	0	0.5	0.1	6.3
Sample A (75 ppm)	0	0.1	0	10.3	14.2
DNBP (500 ppm)	0	0.1	0.5	1.5	-
DNBP (300 ppm)	0	0	1	2	3.6
DNP (500 ppm)	0	0.2	0.5	0.8	-
DNP (300 ppm)	0	0.5	0.9	1.5	

The data in The Table show that the inhibitors of the present invention have superior activity to inhibitors of the prior art. The instant inhibitors have the same activity as DNBP or DNP but at one third the concentration.

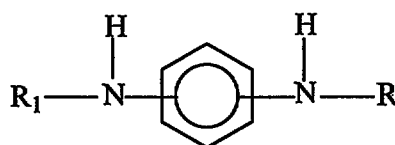
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CLAIMS:

1. A process for inhibiting the polymerization of a vinyl aromatic compound during distillation of the vinyl aromatic compound comprising adding to the compound an effective amount of the reaction product of nitrous acid and an amine having the formula:
- 5

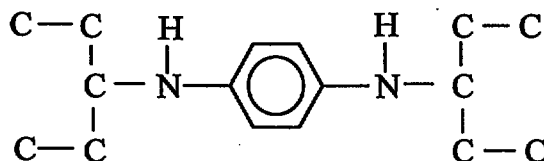


where R and R_1 are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

10

2. The process of claim 1 where R and R_1 are each selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl, sec-butyl, iso-propyl and iso-pentyl.

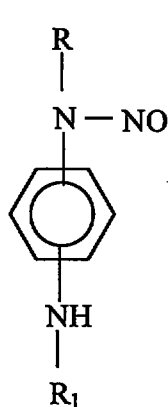
3. The process of claim 2 where the amine is
- 15



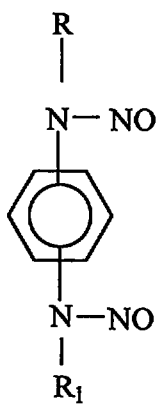


4. The process of claim 1 where the vinyl aromatic compound is selected from the group consisting of styrene, alpha-methyl styrene, divinylbenzene, vinyl toluene, vinyl naphthalene and polyvinylbenzene.

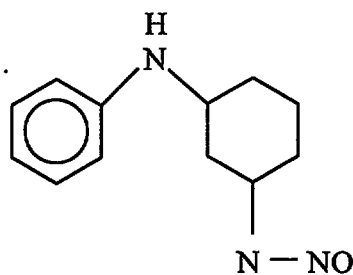
5. A process for inhibiting the polymerization of a vinyl aromatic compound during the distillation of the vinyl aromatic compound comprising adding to the compound an effective amount of a nitroso compound selected from the group consisting of:



(I)



(II)



(III)

10

and mixtures thereof and R and R₁ are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

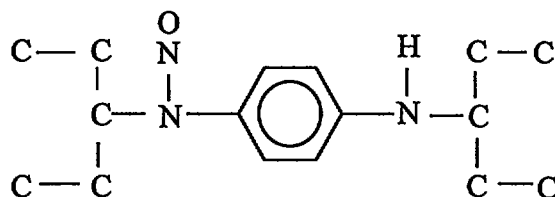
6. The process of claim 5 where the nitroso compound is a mixture of compound I and II.





7. The process of claim 5 where R and R₁ are each selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl, sec-butyl, iso-propyl and iso-pentyl.

8. The process of claim 5 where the nitroso compound is



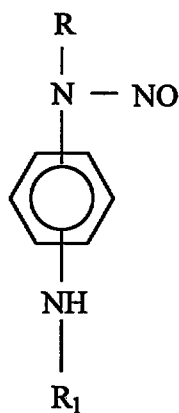
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9. The process of claim 5 where the nitroso compound is added as a mixture of inhibitor compounds having structures I, II and IV:

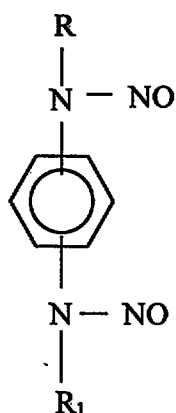
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where R and R₁ are each hydrogen or an alkyl group having from 1 to 18 carbon atoms.

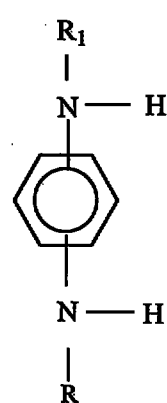




(I)



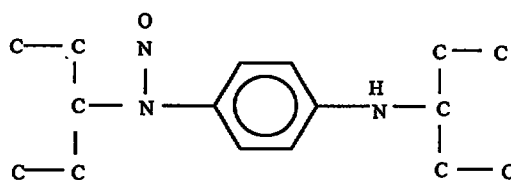
(II)



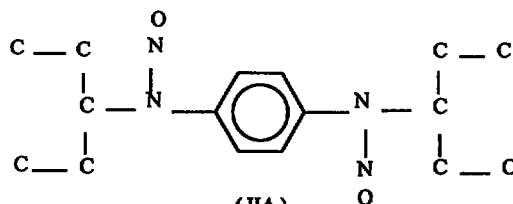
(IV)

10. The process of claim 9 where the amount of compound I varies from 18 to 96 wt.%, the amount of compound II varies from 2 to 50 wt.% and the amount of compound IV varies from 2 to 80 wt.%.
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11. The process of Claim 9 where compounds I, II and IV have structures IA, IIA and IVA:

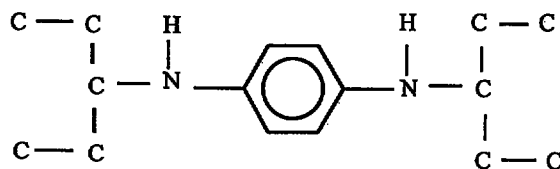


(IA)



(IIA)





(IV A)

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